Technical Letter

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On disinfection of remineralised waters

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Author: Manuel Hernández, Ph.D., M.Sc., Dipl. Ing.

1. Introduction

The process of chlorination is extensively dealt with in the literature, despite which the handling of the remineralisation process to subsequently guarantee proper disinfection frequently elicits questions among the operators of desalination plants.

In Spain, the health inspectors, on the basis of the regional standards and also of the recommendations of the World Health Organisation's Guideline for Drinking Waters (WHO, 1993, 2004, 2007 and 2011), recommend a dose of free residual chlorine of > 0.5 mg/L after 30 minutes of contact time in the water, and a pH below 8.

Remineralised water generally has a pH of more than 8 and does not, therefore, meet the pH requirement for water chlorination.

The reasoning of the plant operators for considering to lower pH below 8 is normally as follows: desalinated water is already free from virus and bacteria and also from metals and organic matter, so why do I have to produce water with a pH of less than 8?

This chapter first summarises the reasons of why it is recommended that the pH of the water be below 8 prior to disinfection.

Then, it describes the demand for chlorination of remineralised waters on the basis of existing information.

Also presented is a simulation of the required dosing with CO_2 and NaOH to maintain a remineralised water with a pH < 8.

In view of the fact that remineralised water continues to have a low buffering capacity and that its pH changes easily when subjected to prolonged aeration, data from a simulation are also presented to illustrate this effect.

Finally, a table with $CaCO_3$ and CO_2 consumption and costs depending on pH objectives is presented.

2. Disinfection at different values of pH

There are numerous publications that provide evidence of the reduction of the lethal effect of residual chlorine on bacteria and virus with pH values higher than 8.

This reduced efficiency is due to the alteration that free residual chlorine undergoes at high pH values. Free residual chlorine, which is the sum of the two forms of chlorine: HClO (more lethal) + OCl^- (less lethal), depends on pH. At high pH values, the free residual chlorine is in the form of OCl, the less lethal. Figure 2.1 illustrates this aspect.

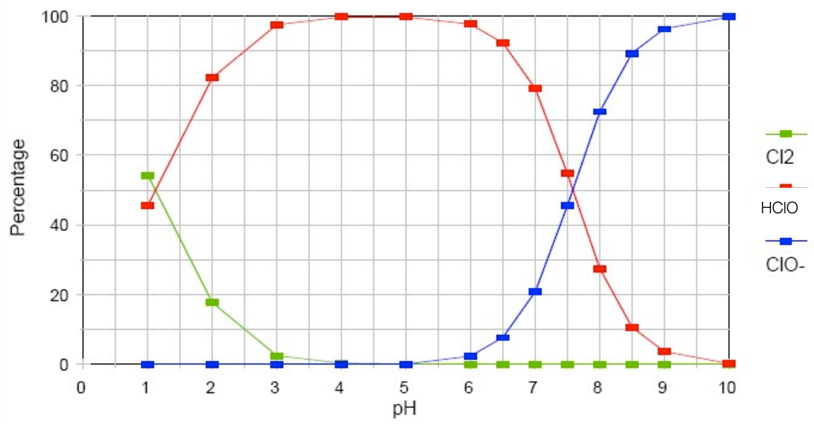

Fig. 2.1: Distribution of free residual chlorine species with pH.

TABLE 2.1: EFFICIENCY OF FREE RESIDUAL CHLORINE DEPENDING ON PH (% SURVIVAL) (FRIBERG ET. AL, 1956)

pH	4.5	5	5.5	6	6.5	7	7.5	8	8.5
Efficiency	100%	100%	99%	97%	95%	92%	85%	18%	6%

The results of Table 2.1 also show that for a pH > 8 the efficiency of HClO disinfection decreases below 18%.

To increase the efficiency of the disinfection at high pH values, it is recommended that free chlorine dose and contact time are increased. Contact time (in minutes) by free residual chlorine dose (in mg/L) is known as TC.

For a water with a pH = 8, the US EPA (Guideline 1989) recommends a TC = 60 in order to guarantee a 99.9% reduction of *Giardia lambia*.

Table 2.2 shows the contact time and free residual chlorine concentration recommendation to be considered with increasing pH according to Taschenbuch der Wasserversorgung, 12ed. 2002,

TABLE 2.2: CONCENTRATION OF RESIDUAL CHLORINE (MG/L) DEPENDING ON PH (TASCHENBUCH DER WASSERVERSORGUNG, 12ED. 2002)

Contact time (min)	pH 6	pH 7	pH 8
5	0.3	0.4	0.7
10	0.2	0.2	0.4
15	0.1	0.15	0.25
30	0.05	0.06	0.12
45	0.04	0.04	0.06
60	0.03	0.03	0.06

3. Resistance to chlorine of *Legionella pneumophila*

The bacterium *Legionella pneumophila* is much more resistant to chlorine than *Escherichia coli*.

Kuchta et. al (1983) demonstrated that for a water at 21ºC, with a pH of 7.6 and 0.1 mg of free residual chlorine, at least 40 minutes are required to eradicate 99% of *L. pneumophila*, while under the same conditions less than 1 minute is sufficient for *Escherichia coli.*

As is shown in Figure 3.1 (Kuchta et. al, 1983), with 0.1 mg/L of free residual chlorine, more than 60 minutes of contact were required to guarantee a 99.9% bactericide effect on *L. pneumophila* with a pH in excess of 7.6.

As is shown in Figure 3.2, the efficiency of application varies with temperature. For desalination facility water at a temperature of between 18ºC and 24ºC, contact time must be around 60 minutes.

In their work on the disinfection of waters at hospitals, Yun-sen E.Lin et. al (1998) observed that with 0.4 mg/L of free residual chlorine and a contact time of 15 minutes, inactivation of the *L. pneumophila* in suspension was achieved, this not being the case for that adhering to the walls of the piping.

It is important to underline the fact that all the Spanish standards and technical documentation reviewed dealing with the prevention of *legionellosis* (Spanish RD 865/2003; WHO (2007); OSHA (1999) and the recommendations for the prevention and control of *legionellosis* issued by the Technical Secretariat General of the Spanish Ministry of Health and Consumption (1999) urge that a pH< 8 be maintained throughout the stipulated contact time.

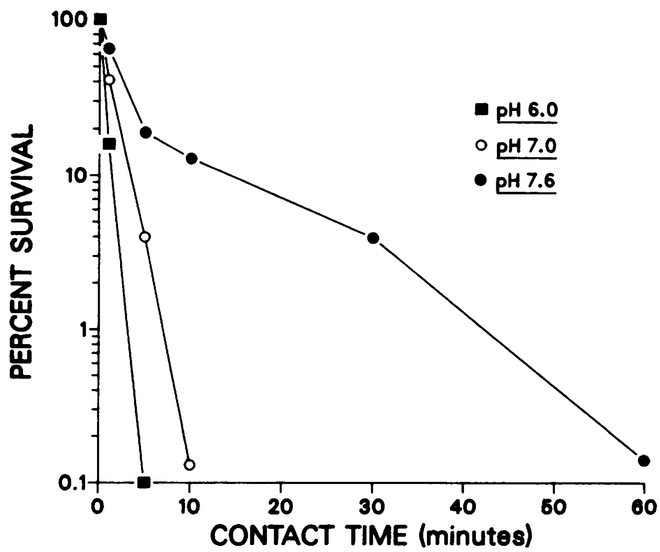

Fig. 3.1: Effect of pH on bactericide activity of 0.1 mg of chlorine per litre on *L pneumophila* in tap water at 21ºC (Kutcha et. al, 1983).

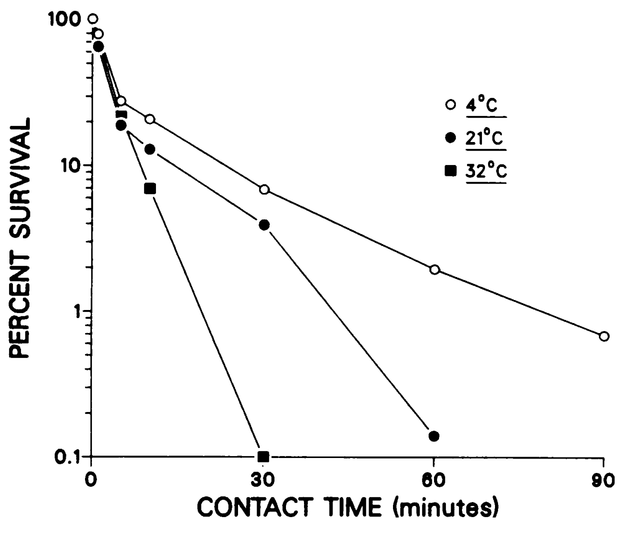

Fig. 3.2: Effect of temperature on bactericide activity of 0.1 mg of chlorine per litre on *L pneumophila* in tap water at different temperatures and pH of 7.6 (Kutcha et. al, 1983)

4. Chlorine demand of remineralised water

Desalinated waters are free from virus and bacteria, metals and organic compounds. However, remineralised waters may be affected by bacterial contamination of the calcite and also, albeit to a minimum extent, by organic contamination. Nevertheless, in practice it is assumed that in the disinfection of remineralised waters all the chlorine added is converted into free residual chlorine.

This is suggested by work performed by Guadalupe Daza (Cadagua, Ceuta Desalination Plant, p.c., 2013) and Jordi Romero (Agbar, Sant Joan Despí ETAP), p.c., 2013).

Both Figure 4.1, which compares schematically the evolution of free residual chlorine depending on chlorine dose, and Figure 4.2, which compares the drop in free residual chlorine over time for different types of water, have been plotted on the basis of this work.

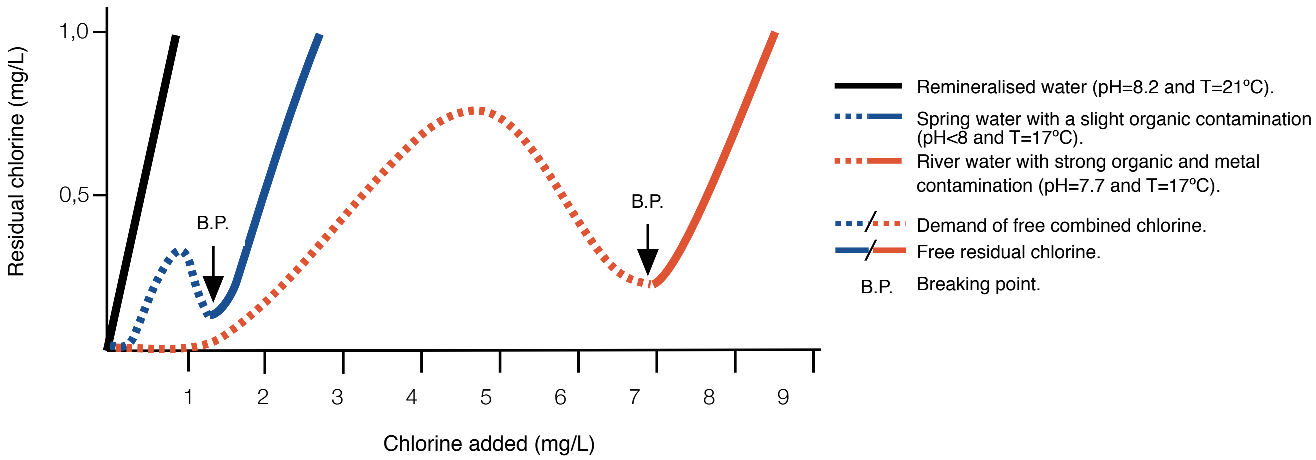

Fig. 4.1: Evolution of residual chlorine following a dose of 1 mg Cl/L and for different types of waters

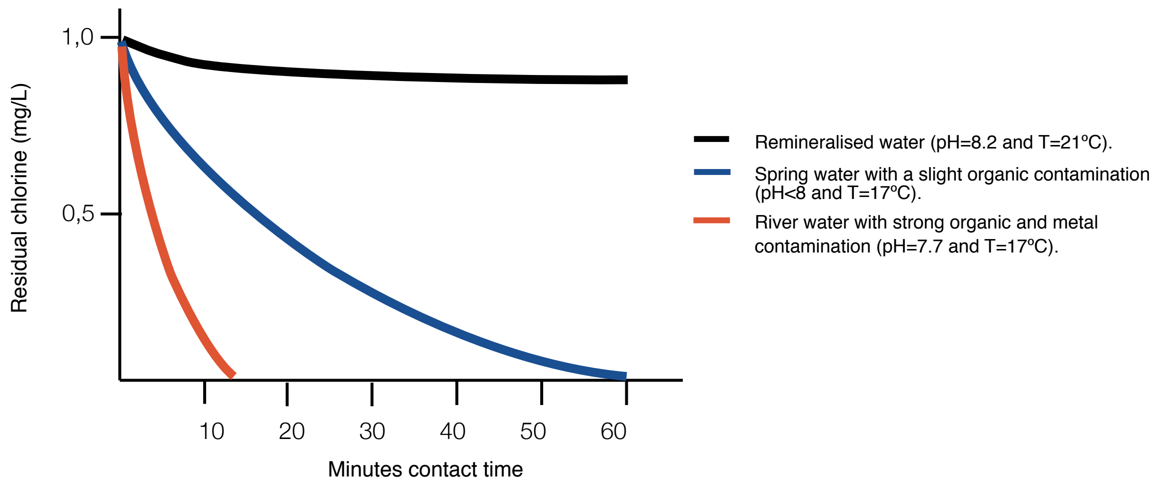

Fig. 4.2: Efficiency of disinfection of remineralised water (% survival) with and without final dosing with NaOH and for a positive LSI.

At this juncture it should be pointed out that the bibliography on the effect of water hardness on the efficiency of chlorination has been reviewed. It may be concluded that in the ranges of hardness in which work is performed with remineralised water <150 mg $CaCO_3$/L there is no effect on chlorination.

5. Efficiency of disinfection depending on remineralisation treatment

Generally speaking, the factors that most favour the multiplication of *L. pneumophila* are high temperatures, soiling, corrosion and incrustations.

Corrosion contributes to the multiplication of *L. pneumophila* by supplying nutrients (iron, phosphates, etc.), thereby favouring bacterial growth. Consequently, corrosion may be a cause of the reduced efficiency of cleaning and disinfection tasks.

For this reason, it is normal to find remineralisation requirements demanding a slightly positive LSI.

This requires the pH to be increased following remineralisation treatment with calcite, this normally being accomplished by dosing with NaOH.

As is indicated in Table 5.1, for cases requiring a positive LSI, the CO_2 dose should be increased to at least 40 mg/L in order for the remineralised water to conserve a pH lower than 8, even after the addition of a minor dose of NaOH (column 6).

Table 5.1 refers to remineralisation for a treated water with a calcite bed with a particle diameter of 2-4 mm and a water with 160 mg TDS/L; pH 6.13; 0.8 mg CaCO3/L; 0.5 mg Ca/L and a temperature of 21ºC, after an EBCT of 11 minutes.

Evidently, these CO_2 doses must be adjusted depending on the characteristics of the permeate water: pH, TDS, Ca, HCO_3 and T. Also approximately a 90% CO_2 application efficiency should be considered

Although it is not particularly significant, it should also be mentioned that a dose of 1 mg NaOCl/L increases pH by approximately 0.05 units in remineralised water.

TABLE 5.1: ESTIMATION OF THE EFFICIENCY OF REMINERALISED WATER DISINFECTION (% SURVIVAL) WITH AND WITHOUT NAOH DOSING TO OBTAIN A POSITIVE LSI (SEE TEXT FOR DETAILS).

CO_2 dose (mg/L)	pH after $CaCO_3$ (EBCT: 11 min)	LSI (EBCT: 11 min)	Efficiency of disinfection after $CaCO_3$ (at pH 7≈ 92%)	NaOH dose mg/L for LSI :+ 0.1	pH after $CaCO_3$ + NaOH	Efficiency of disinfection after $CaCO_3$ + NaOH (at pH 7≈ 92%)
0	9.82	0	≈ 0%	0	9.82	≈ 0%
10	8.77	0	≈ 0%	0	8.87	≈ 0%
15	8.56	-0.05	≈ 6%	0.35	8.71	≈ 0%
20	8.3	-0.1	≈ 15%	0.45	8.51	≈ 6%
25	8.13	-0.13	≈ 22 %	0.55	8.34	≈ 13 %
30	7.96	-0.15	≈ 34%	0.8	8.21	≈ 20 %
40	7.75	-0.16	≈ 55%	1.4	8	≈ 28%
50	7.58	-0.18	≈ 78%	2.35	7.84	≈ 40%

6. Effect of prolonged aeration on the pH and LSI of remineralised water

A prolonged aeration of >2 hours of the remineralised water accompanied by agitation implies the exchange of CO_2 with the atmosphere.

The CO_2 doses shown in Table 5.1 refer to a water not subjected to aeration following remineralisation or the addition of NaOH. Nevertheless, aeration and shaking facilitate the exchange of CO_2 with the atmosphere, this varying pH.

Table 6.1 illustrates approximately the changes in pH that may occur in these cases. As it is indicated, consideration should be given to losses of CO_2, especially when CO_2 dosing is higher than 30 mg/L.

On the other hand, and according to the criteria prevailing in the literature, significant precipitation of $CaCO_3$ in remineralised water starts to occur when LSI > 0.5 and pH ≥ 8.4.

TABLE 6.1: EFFECT OF PROLONGED AERATION ON THE PH AND LSI OF REMINERALISED WATER.

CO_2 dose mg/L	pH after $CaCO_3$ (EBCT: 11 min)	LSI (EBCT: 11 min)	pH after prolonged aeration (> 2 h)	LSI after prolonged aeration (> 2 h)
0	9.82	0	7.53	-1.96
10	8.87	0	7.88	-0.96
15	8.59	-0.05	8.01	-0.58
20	8.3	-0.1	8.13	-0.27
25	8.13	-0.12	8.19	-0.06
30	7.96	-0.15	8.21	+0.10
40	7.75	-0.16	8.21	+0.30
50	7.59	-0.17	8.21	+0.45

7. Effect of increasing dose of CO_2 and $CaCO_3$ on treatment costs

Table 7.1 illustrates the estimated costs of remineralisation in Euro cents and depending on CO_2 dose. The simulation has been performed for the same water as of Table 5.1. The assumed price of the CO_2 amounts to 0.31 €/kg and that of the $CaCO_3$ to 0.1 €/kg. As can be seen costs increase significantly when dose increases from the normal 25 mg CO_2/L to 40 mg CO_2/L required for complying with pH and positive LSI conditions.

TABLE 7.1 ESTIMATION OF POST-TREATMENT COST DEPENDING ON CO_2 AND $CaCO_3$ DOSE.

CO_2 dose mg/L	Consumption of $CaCO_3$ mg/L	Cost of CO_2 cts/m³ (assuming 0.31 €/kg CO_2)	Cost of $CaCO_3$ cts/m³ (assuming 0.1 €/kg $CaCO_3$)	Total remin. cts/m³	Total for 1.000 m³/d plant (€/year)
0	12.6	0	0.126	0.126	460
10	28.1	0.31	0.281	0.591	2,157
15	38.3	0.465	0.383	0.848	3,095
20	48.5	0.62	0.485	1.105	4,033
25	58.7	0.775	0.587	1.362	4,971
30	68.5	0.93	0.685	1.615	5,895
40	87.6	1.24	0.876	2.116	7,723
50	104.8	1.55	1.048	2.598	9,483

8. Conclusions regarding disinfection of remineralised water and CO_2 dose

The analysis performed indicates that dosing with at least 30 mg CO_2/L is necessary to maintain the pH of the remineralised water below 8.

Furthermore, if a positive LSI is to be obtained, the dose must be of at least 40 mg CO_2/L in order to counteract the effect of the NaOH.

In addition a 10% increase of those values might have to be considered to account for CO_2 application efficiency.

Interaction between the remineralised water and the atmosphere may increase the pH of the water and, therefore, affect the efficiency of the chlorination.

Thus, the characteristics of each case should be studied and the pH in the distribution network should be monitored in order to check whether chlorination may be affected.

Assuming that a calcite appropriate for use in drinking water is being used, not contaminated with animal excrement, oils, etc., it may be stated that the remineralised water has a very low demand for combined chlorine, since it should not contain metals, organic materials, bacterial or virus contamination.

Consequently, practically all the chlorine added becomes free residual chlorine.

In view of this, a dose of 0.8 to 1.0 mg/L should be considered sufficient when the pH of the water is between 7.9 and 8 and the contact time is > 30 minutes.

Although soiling and the presence of organic matter is not a problem in desalinated waters, the corrosion present in the network caused by deficient remineralisation may serve as a cultivation medium for the development of a bacterial population, especially of *L. pneumophila.*

For these cases, in addition to maintaining a positive LSI and a pH < 8, chlorine dosing must be around 1 mg/L and contact time preferably 1 hour.

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