

Hypochlorous acid loss from neutral electrolyzed water and sodium hypochlorite solutions upon storage

Influência da estocagem na perda de ácido hipocloroso de soluções de água eletrolisada neutra e soluções de hipoclorito de sódio

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■ Summary

The hypochlorous acid (HOCl) loss from electrolyzed water (EW) and sodium hypochlorite (NaOCl) solutions were examined during storage at different temperatures under open conditions and diffused lighting. This work showed that between 25 and 40 °C the kinetics of chlorine loss for either NaOCl solutions or EW was not affected by temperature and that the chlorine loss followed first-order kinetics. This may be because the primary mechanism of chlorine loss could be evaporation rather than the self-decomposition of the chlorine species. By the equations presented in this work, pH can be used to determine the HOCl concentration. HOCl loss is faster in a NaOCl solution than in EW solutions. Storage time and pH affect more significantly HOCl loss from a NaOCl solution than from EW.

Key words: *Electrolyzed water; Decomposition kinetics; Temperature; pH.*

■ Resumo

A perda de ácido hipocloroso (HOCl) presente em água eletrolisada e em soluções de hipoclorito de sódio foi avaliada durante a estocagem em recipientes abertos em temperaturas entre 25 e 40 °C. Os resultados desse trabalho mostraram que a constante da velocidade de decomposição do HOCl, independente de sua origem, não é afetada na faixa de temperatura de estocagem estudada e segue uma cinética de primeira ordem, provavelmente, porque o principal mecanismo que provoca a perda de cloro é a evaporação e não a autodecomposição. A partir das equações apresentadas nesse trabalho, o pH pode ser usado para determinar a concentração de HOCl. A perda de ácido hipocloroso é mais rápida em soluções de NaOCl do que em água eletrolisada.

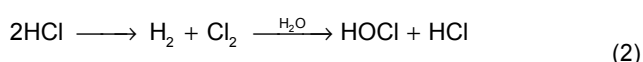
Palavras-chave: *Água eletrolisada; Cinética de perda de HOCl; Temperatura; pH.*

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1 Introduction

Bacterial contamination on food-processing surfaces that results in food spoilage or transmission of disease has been extensively reported. The use of sanitizers such as chlorine, peracetic acid and quaternary ammonium compounds by the food industry is aimed at reducing microbial numbers to safe levels. Although several commercial products are available, research is still being conducted searching for new techniques and technologies. A recent development is the use of acidic electrolyzed water (AEW) or neutral electrolyzed water (NEW) as sanitizers (AL-HAQ *et al.*, 2005). Electrolyzed water (EW) is produced by passing a dilute salt (NaCl) or acid (HCl) solution through an electrolytic cell and it has recently been introduced to food industries as a novel sanitizer agent. Len *et al.* (2002) suggested that the active bactericidal agent is hypochlorous acid (HOCl) formed by the hydrolysis of electrochemically produced chlorine gas (Cl_2) as shown in Reaction 1 (LEN *et al.*, 2002) or by hypohydrochloric acid electrolysis as shown in acid Reaction 2.



Evidence exists that electrolyzed water can work better than chlorine solutions as a sanitizer (AL-HAQ, 2005) and that sanitation with EW is more convenient than conventional chlorine sanitation for the following reasons (IZUMI, 1999; SAPERS, 2001; PARK *et al.*, 2002a; PARK *et al.*, 2002b; DEZA *et al.*, 2003; AYEBAH *et al.*, 2005; BOSILEVAC *et al.*, 2005; AL-HAQ *et al.*, 2005; DEZA *et al.*, 2005): it can be produced on-site; its use reduces the cost and hazards associated with the handling, transportation and storage of concentrated chlorine solution; it is more environment-friendly; it reverts to normal water after use, without releasing large amounts of harmful gases such as chlorine; some researchers claim that microorganisms do not acquire resistance to EW; it could be used to rinse fruits, vegetables, meat and poultry for eliminating or substantially decreasing bacterial population; several reports have demonstrated that operational expenses related to bactericidal effect of EW on pathogenic bacteria and biofilms are minimal; EW does not change the food's organoleptic properties. On the other hand the disadvantages include: its effectiveness is reduced by the presence of protein; the initial purchase of the equipment may be costly; with time, the bactericidal activity of stored EW is reduced over time due to chlorine loss; EW contains free chlorine, which can damage plant tissue.

One of the limitations of EW is its loss of bactericidal activity over time, which is caused by chlorine (Cl_2) loss due to the evaporation of dissolved chlorine gas and

ensuing hypochlorous acid (HOCl) decomposition as shown in Equation 1 (AL-HAQ *et al.*, 2005). These authors showed that the free chlorine content of EW dropped significantly (by 80%) after 120 min under stirring storage. Len *et al.* (2002) reported that under open conditions, the chlorine in EW was completely lost after 30 h when agitated and after 100 h when not agitated. The same authors also reported that the chlorine loss rate constant under open storage was not affected by artificial light (light from 40 W fluorescent lamps). They also observed that under open storage conditions the chlorine loss follows first-order kinetics because the primary mechanism of chlorine loss may be the evaporation of chlorine. The first-order kinetics for chlorine evaporation is not applicable for closed storage conditions. The primary mechanism of chlorine loss under closed conditions could be the self-decomposition of the chlorine species in the solution, because chlorine evaporation was limited. Because of this decomposition, a reduction in the efficacy of EW as a sanitizer is observed.

The objective of this study was to examine the chlorine loss of EW under open storage at different temperatures and static conditions.

2 Material and methods

2.1 Preparation of electrolyzed water (EW) and hypochlorous acid solution

EW was prepared by the electrolysis of a 3.0% HCl solution using a commercial EW generator (model Mp-240E, Morinaga Purester, Tokyo, Japan) with an EW production capacity of 240 L/h. The pH and the active chlorine concentration of EW were measured as HOCl.

This EW generator (Mp-240E) uses an electrolytic cell without diaphragm. With this method the water generated by the positive and negative poles were not physically separated thus generating a neutral electrolyzed water solution.

Hypochlorous acid (HOCl) solutions obtained by NaOCl were prepared by appropriately diluting a 4-6% sodium hypochlorite solution (Vetec, São Paulo, Brazil). The pH and active chlorine concentration of NaOCl solutions was measured as HOCl.

2.2 Effect of storage

Volumes of 700 mL of hypochlorous acid solutions were maintained in 1000 mL Erlenmeyers at constant temperatures (25, 30, 35 and 40 °C) by means of a thermostatic bath and under a 650 lux lighting obtained from fluorescent lamps. Their pH and hypochlorous acid concentrations were measured at regular intervals. At least three independent Erlenmeyer flasks were used for each storage temperature.

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2.3 Analytical measurements

The concentrations of hypochlorous acid in EW solutions were measured using the iodometric methodology (APHA, 1998) and the pH was measured using a pHmeter (model B474, Micronal). A mass of 90.0 to 100.0 g of the solution was transferred to a 500 mL Erlenmeyer and a 0.01 N sodium thiosulphate was used to determine the HOCl concentration.

All the figures and mathematical equations were obtained using the Origin 6.0 software.

3 Results and discussion

Each point shown in Figures 1 and 2 is the average of three to five independent assays and represents the relation (F) between an actual hypochlorous acid concentration and the initial hypochlorous acid concentration ($\text{HOCl}/\text{HOCl}_0$) obtained from NaOCl solutions and EW, respectively. The initial concentration for both solutions was $20.0 \text{ mg}\cdot\text{L}^{-1}$. Results show that the concentration of hypochlorous acid either for EW or sodium hypochlorite solutions decreases with time. As storage in the temperature of range of 25-40 °C had no significant effect ($p \geq 0.05$) on chlorine loss, average values were calculated for each point in Figures 1 and 2 and are shown on Table 1 and Figure 3. It was confirmed that the chlorine loss followed first-order kinetics as observed by Len et al. (2002). As observed by these authors the first-order kinetics based on chlorine evaporation was applicable for open storage condition.

It is observed that the rate constant for chlorine loss was larger for hypochlorous acid present in sodium hypochlorite solution ($5.28 \cdot 10^{-3} \text{ h}^{-1}$) than for EW ($2.45 \cdot 10^{-3} \text{ h}^{-1}$). The chlorine loss for both sources can be represented by an Equation 1 of the type:

$$F = F_{\infty} + F_{0-\infty} \cdot e^{-k \cdot \theta} \quad (1)$$

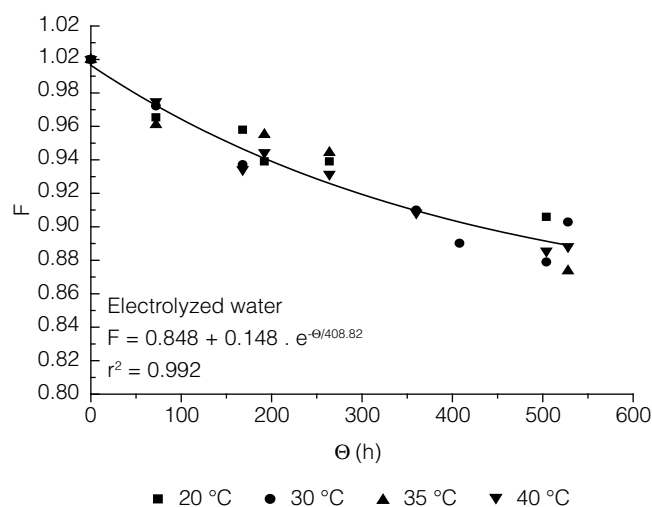


Figure 1. Values of F for storage of EW solutions at different temperatures.

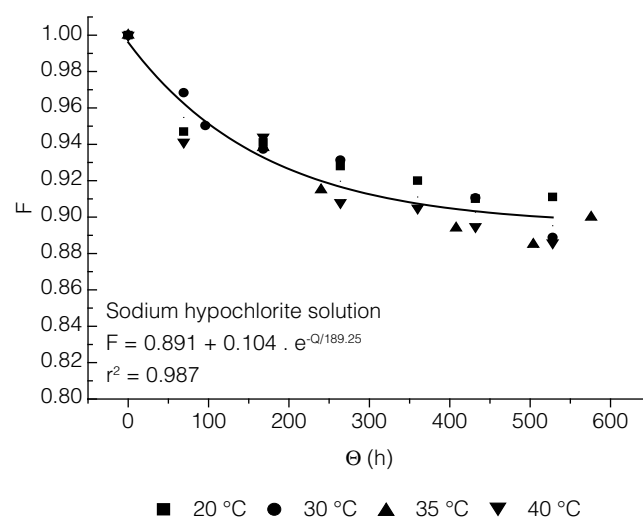


Figure 2. Values of F for storage of NaOCl solutions at different temperatures.

Table 1. Means and standard deviations for the ratios of hypochlorous acid concentration to the initial hypochlorous acid concentration ($\text{HOCl}/\text{HOCl}_0$) for EW and NaOCl solutions.

NaOCl solutions			Electrolyzed water		
Storage time (h)	Mean of F	Standard deviation	Storage time (h)	Mean of F	Standard deviation
0	1.0000	0.0000	0	1.0000	0.0000
69	0.9548	0.0192	72	0.9669	0.0048
96	0.9503	0.0154	168	0.9440	0.0304
168	0.9372	0.0143	192	0.9417	0.0038
264	0.9197	0.0110	264	0.9316	0.0002
360	0.9111	0.0138	360	0.9084	0.0027
432	0.9027	0.0069	408	0.9042	0.0202
528	0.8953	0.0138	504	0.8902	0.0410
-	-	-	528	0.8882	0.0028

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Equation 1 results from a mathematical fitting of the experimental data presented in Figures 1 and 2, where F is the hypochlorous acid fraction, F_{∞} is the relation between hypochlorous acid concentration and the initial hypochlorous acid concentration at infinite time, and $F_{0-\infty}$ is the difference between $(HOCl/HOCl_0)$ at the beginning of storage and F_{∞} , k is the hypochlorous acid decomposition rate constant (h^{-1}) and Θ is the storage time (h).

Table 2 shows F_{∞} , $F_{0-\infty}$, and k values for sodium hypochlorite solutions and EW. This table shows that

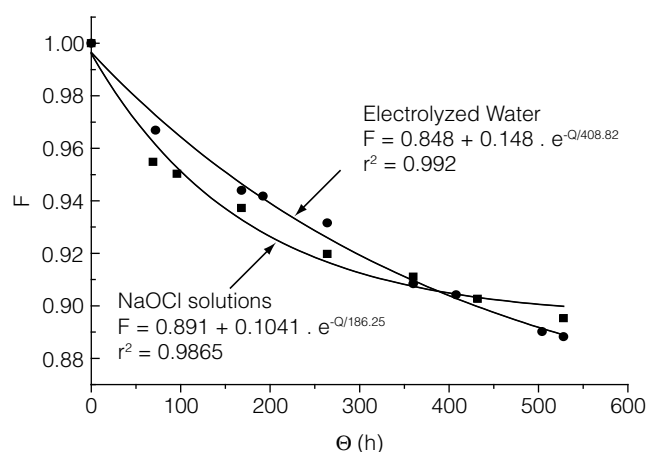


Figure 3. Values of F for EW and HOCl solutions at different temperatures.

Table 2. F_{∞} , $F_{0-\infty}$ and k values for sodium hypochlorite and EW solutions.

Solution	F_{∞}	$F_{0-\infty}$	k (h^{-1})
EW	0.848	0.148	$2.45 \cdot 10^{-3}$
NaOCl	0.891	0.104	$5.28 \cdot 10^{-3}$

maximum hypochlorous acid concentration variations were 15% for EW and 10% for sodium hypochlorite solutions.

Len et al. (2002) in their work observed that at 25 °C and under open and static conditions, the chlorine in EW was completely lost after 100 h. It was also noted that under closed conditions lighting was a more important factor than agitation for chlorine loss. When room illumination was applied, approximately 60% of the chlorine was lost after 1400 h, as compared to about 40% under dark conditions, suggesting that diffused light induces the self-decomposition of chlorine during storage. In either open or closed conditions the chlorine loss observed by Len et al. (2002) was greater than that observed in this work. This study shows that after 100 h of storage under closed and static conditions, the loss of HOCl is 4% for EW and 5% for NaOCl solution. This difference can possibly be explained because the solution used by Len et al. (2002) had a pH of 2.5, while the EW generator used in this work produced an EW solution with initial a pH of 6.7, whereas at $pH > 6.0$ the predominant chlorine species in solution is not chlorine gas, but HOCl and OCl^- . (JENNINGS, 1965). Therefore, chlorine loss due to the evaporation of dissolved chlorine gas is significantly reduced at these higher pH values, thus resulting in a greater stability of the species. Len et al. (2002) have shown that the chlorine losses of EW and chlorinated water after 250 h of storage at pH 6.0 and 9.0 were not significantly different from each other, but were less than those observed in acidic media.

Table 3 and Figure 4 show the average values of three independent measurements of pH variations for EW and sodium hypochlorite solutions with a standard deviation of 0.11. These variations follow a zeroth-order model (Equation 2), but for EW solutions the pH variation

Table 3. Means and standard deviations for F_{pH} values.

NaOCl solutions			Electrolyzed water		
Storage time (h)	F_{pH}	Standard deviation	Storage time (h)	F_{pH}	Standard deviation
0	1.0000	0.0000	0	1.0000	0.0000
72	1.0079	0.0173	96	0.9935	0.0128
144	1.0360	0.0211	168	0.9891	0.0136
168	1.0326	0.0218	240	0.9826	0.0174
240	1.0546	0.0206	264	0.9840	0.0182
336	1.0743	0.0205	336	0.9721	0.0264
360	1.0773	0.0333	360	0.9748	0.0087
408	1.0820	0.0131	432	0.9656	0.0130
504	1.1068	0.0280	528	0.9582	0.0086
576	1.1165	0.0173	624	0.9523	-
600	1.1190	0.0393	648	0.9564	0.0124
624	1.1287	-	768	0.9460	0.0085
672	1.1431	0.0350	-	-	-
768	1.1485	0.0073	-	-	-

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is increasing, while for sodium hypochlorite solutions the pH values are decreasing. The initial pH values for these solutions were 6.66 for EW, and 8.39 for the NaOCl solution. The mathematical Equations 3 and 4 result from the fitting of the experimental data that represent the pH variations for EW and for sodium hypochlorite solution, respectively. F_{pH} is the relation between pH and initial pH, Θ represents the storage time and the angular coefficients of Equations 2 and 3 can not be considered as being zero ($p \leq 0.05$).

$$F_{pH} = F_{pH_0} + k \cdot \Theta \tag{2}$$

$$F_{pH} = 1.00 + 2.02 \cdot 10^{-4} \cdot \Theta \tag{3}$$

$r^2 = 0.995$

$$F_{pH} = 1.00 - 7.31 \cdot 10^{-5} \cdot \Theta \tag{4}$$

$r^2 = 0.990$

Figure 5 shows the correlations between the variations of hypochlorous acid concentration with pH. Hypochlorous acid concentration in EW solutions decreased with increasing pH. On the other hand, as the pH of the sodium hypochlorite solutions increased, the HOCl concentration also increased, just as observed by Len et al. (2002). The mathematical equations representation for F with F_{pH} are (5) for EW and (6) for sodium hypochlorite solutions. Equations 5 and 6 are important in food industries for on line concentration control using a pHmeter.

$$F = 8.62 \cdot 10^{-1} + \frac{4.80 \cdot 10^{-4}}{4 \cdot (F_{pH} - 9.20 \cdot 10^{-1})^2 + 1.05 \cdot 10^{-2}} \tag{5}$$

$r^2 = 0.980$

$$F = 8.85 \cdot 10^{-1} + \frac{2.04 \cdot 10^{-4}}{4 \cdot (F_{pH} - 1.02)^2 + 3.86 \cdot 10^{-5}} \tag{6}$$

$r^2 = 0.996$

Figure 5 shows that a pH variation of 10%, from 1.00 to 1.10, causes a 10% variation in the concentration of hypochlorous acid in EW from 1.00 to 0.90. In order to have the same loss in hypochlorous acid in a sodium hypochlorite, a variation of only 4% in the pH (like from 1.00 to 0.96), would suffice. Therefore, the influence of pH upon HOCl, in relation to a NaOCl solution is 2.5 greater than on EW.

Figures 6 and 7 show the influence of pH and relation between hypochlorous acid concentration and initial hypochlorous acid concentration ($HOCl/HOCl_0$). Here it can be observed that the variation of F value for the same F_{pH} value, for both solutions, is smaller at the end

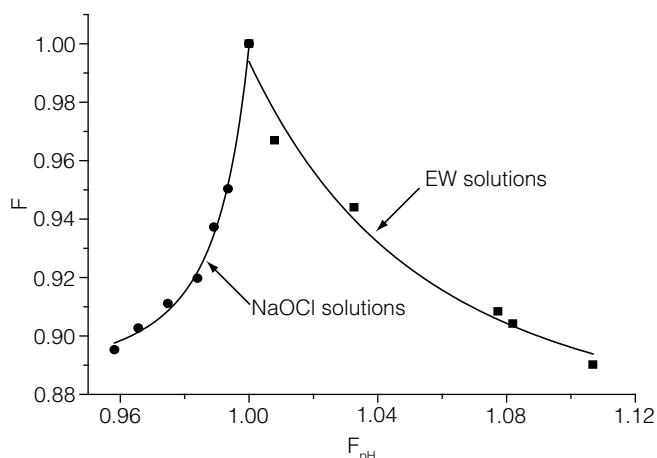


Figure 5. Correlations between F and F_{pH} for EW and sodium hypochlorite solutions.

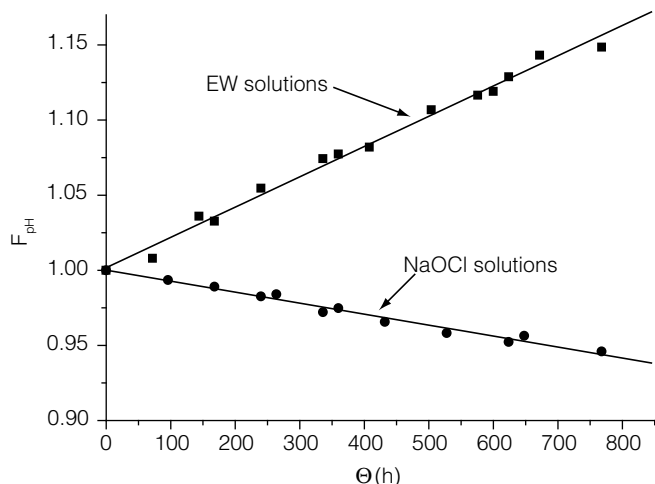


Figure 4. Values of F_{pH} for EW and in sodium hypochlorite solutions.

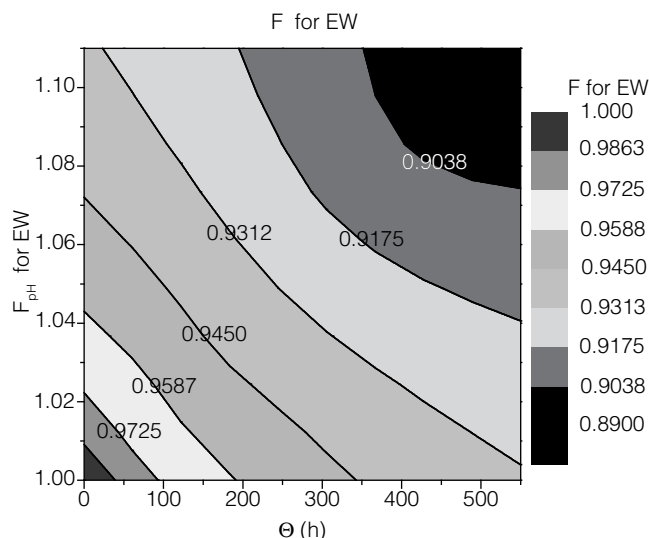


Figure 6. Influence of storage time on F and F_{pH} for EW.

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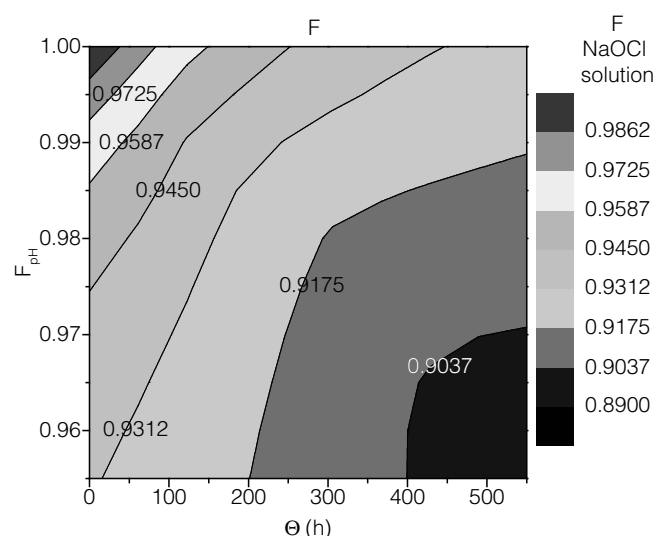


Figure 7. Influence of storage time on F and F_{pH} for EW and NaOCl solution.

than at the beginning of the storage. For instance, with an F_{pH} value of 1.02 190 h are necessary to decrease F from 0.9450 to 0.9312, but only 100 h to decrease F from 0.9725 to 0.9587.

4 Conclusions

This work has shown that HOCl loss in the range of 25 and 40 °C is independent of temperature either in EW or a NaOCl solution. At the age conditions tested during this work the chlorine loss followed first-order kinetics. pH can be used to determine the HOCl concentration by Equations 4 and 5. HOCl loss is faster in the NaOCl solution than in the EW solution. pH affects more significantly HOCl loss in NaOCl solution than in EW.

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Nomenclature

F = relation between a hypochlorous acid concentration and the initial hypochlorous acid concentration ($\text{HOCl}/\text{HOCl}_0$);

F_{∞} = relation between a hypochlorous acid concentration and the initial hypochlorous acid concentration at infinite time;

$F_{0-\infty}$ = difference between ($\text{HOCl}/\text{HOCl}_0$) at the beginning of storage and F_{∞} ;

k = hypochlorous acid decomposition rate constant (h^{-1});

θ = storage time (h);

pH_0 = solution initial pH value solution; and

F_{pH} = relation between pH and initial pH.

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