

An experimental study of an NaClO generator for anti-microbial applications in the food industry

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Received 3 July 2001; accepted 25 September 2001

Abstract

A pilot scale sodium hypochlorite (NaClO) continuous generator is described in this paper, which was used for anti-microbial applications, basically for cleaning-in-place (CIP) or sterilizing-in-place (SIP), in food industry. The electrolytic cell was constructed as a tubular electrochemical reactor with a nylon net membrane between the electrodes and with a layer of rare-earth metallic oxide, RuO₂, as catalytic coating on the titanium-anode surface. The performance of this sodium hypochlorite continuous generator was analyzed from a reaction engineering view point. The electric current efficiency was above 82% and the consumption of sodium chlorine was 2.7 kg for producing 1 kg of available chlorine (Cl₂). The sterilizing water production rate ranged from 810 to 1080 l per hour with an available chlorine concentration of 200–150 ppm. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Sodium hypochlorite; Generator; Cleaning-in-place; Sterilizing-in-place; Electrochemical reactor; Electrolytic cell

1. Introduction

Microbial activity is the main cause of the spoilage and degradation of food products. Keeping the equipment surface clean and uncontaminated is very important to the food industry. Cleaning-in-place (CIP) plays a critical role in quality control programs (Reinemann & Mein, 1997). Sodium hydroxide (NaOH) is a commonly used chemical in CIP in the food, beverage, and dairy industries. However, such CIP procedures found difficulty in removing or inactivating the colonized cells or biofilm cells which developed on solid walls (Flint, van den Elzen, Brooks, & Bremer, 1999). The surviving bacteria can pass into the food materials to be treated, contaminate the food and other surface, and finally threaten the quality of food products. Therefore, in addition to CIP, the authors consider that the concept of sterilizing-in-place (SIP) should attract more attention in the food, beverage and dairy industries.

As a highly effective and low cost biocide, sodium hypochlorite (NaClO) has been one of the most widely used and studied sanitizers. For instance, its anti-microbial kinetics and its anti-microbial behavior to bio-

film cells has been well studied and was best described by the 'stoichiometric transport model' (Borovec, Broumis, Adcock, Fang, & Uren, 1998; Dodds, Grobe, & Stewart, 2000). It is a common household bleach and sanitizer commercially available in supermarket (Racioppi et al., 1994).

In recent years, there have been an increasing number of outbreaks of food poisoning linked to the consumption of vegetables and fruit in developed countries. For instance, the number of reported outbreaks in the USA more than doubled from the period 1973–1987 to the period 1988–1991 (Tauxe, Hedberg, Potter, Madden, & Wachsmuch, 1997). The use of a sanitizer in postharvest treatment (or before consumption) of vegetables to control the pathogenic bacteria has attracted more attentions (Behrsing, Winkler, Franz, & Premier, 2000; Soriano, Rico, Molto, & Manes, 2000; Tournas, 1994; Weissinger, Chantarapanont, & Beuchat, 2000). The general available chlorine (ACH) concentration recommended ranges from 50 to 100 ppm. In this range of ACH concentration, according to our previous study, more than 99% of adhered bacteria could be killed on the solid surface.

In the cleaning of chicken processing equipment in slaughterhouses, utilization of sodium hypochlorite was investigated by Rossoni and Gaylarde (2000) to control

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Nomenclature

C_{ACH}	available chlorine concentration, mg/l (\approx ppm)	Q	electric charge consumed by electrochemical reaction, C
C_{NaCl}	sodium chloride concentration, g/l	V_{NaCl}	volume flow rate of salt water, ml/s
F	Faraday constant, $F = 96485.5$ C	V_B	volume flow rate of bulk water, ml/s
I	electrode current, A	V_T	volume of the standard solution of sodium thiosulfate ($[0.1 \text{ M}] \text{ Na}_2\text{S}_2\text{O}_3$ solution) consumed in the titration of the ACH concentration, ml
M_{Cl_2}	molecular mass of chlorine, $M_{Cl_2} = 71$	η_c	electric current efficiency, %
m_{Cl_2}	mass of chlorine produced by electrochemical reaction, g	η_s	percentage of salt utilization, %
m_{NaCl}	mass of sodium chloride consumed by electrochemical reaction, g	ψ_s	sodium chloride consumption for producing 1 kg chlorine, kg/kg
n_{Cl_2}	number of moles of chlorine produced by electrolysis		
t	time, s		

the growth of *Escherichia coli*, *Pseudomonas fluorescens* and *Staphylococcus aureus* on stainless steel surfaces. The hypochlorite concentration found to be effective for this purpose was 100–250 ppm. In CIP or SIP in the food industry, NaClO also shows efficacy in loosening, removing and inactivating the biofilm cells formed by *Salmonella* spp., *Pseudomonas aeruginosa* and *Staphylococcus epidermidis* on the food contact surface (Eginton, Holah, Allison, Handley, & Gilbert, 1998; Joseph, Otta, Karunasagar, & Karunasagar, 2001). So far, however, the data available in this field is still inadequate.

Sodium hypochlorite can be produced by infusing chlorine gas (Cl_2) into the cold solution of sodium hydroxide or by electrolyzing a salt solution (Bashtan, Goncharuk, Chebotareva, Belyakov, & Linkov, 1999; Horwood, 1980). Unlike chlorine gas, the use of sodium hypochlorite is quite safe and easy to administer. However, concentrated sodium hypochlorite is highly unstable, and the available chlorine in the solution rapidly decreases during storage. This has been studied and modeled to predict the available chlorine concentration after a period of storage (Hua, West, Barker, & Forster, 1999). Therefore, on-site production of sodium hypochlorite by electrolyzing a sodium chloride solution is one method of avoiding this disadvantage.

The biocidal mechanism of ClO^- is due to its strong oxidation property. Hypochlorite is among the most corrosive of chemicals (Craig & Anderson, 1995). This gives it a broad-spectrum anti-microbial efficacy, whilst having the disadvantage of potential corrosion to metal surfaces if the available chlorine concentration exceeds a specified limit. In our experience, it should be controlled under 500 ppm for stainless steel. Under this chlorine concentration, for example, 50–100 ppm for normal application, a quick sterilization treatment of stainless steel, e.g. within 1 h, does not cause measurable corrosion. A long term and intensive study on the initiation and propagation of localized corrosion on stainless steel

by sodium hypochlorite has been carried out (Neville, Hodgkiess, & Destriau, 1998). The corrosion was found to be characterized by crevice and pitting. The weight loss of a 5×5 cm stainless steel sample submersed in 500 ppm chlorine concentration seawater for 2.5 months was 188.1 mg (Abd el Meguid, Mahmoud, & Gouda, 1998; Laycock, Stewart, & Newman, 1997; Neville et al., 1998).

Another problem is the formation of chloroamide when ClO^- combines with amide, since it is suspected to be a potentially carcinogenic substance (Prutz, 1999). However, sodium hypochlorite used for CIP or SIP does not contact with food or food stuff directly, if the surface to be treated is rinsed properly, this risk can be easily eliminated.

In this paper, the set-up of a pilot scale continuous NaClO generator is described. Its main component, a tubular electrochemical reactor, was analyzed from a reaction engineering viewpoint.

2. Experimental principles and apparatus

2.1. Working principle

The system set-up is shown in Fig. 1. When power is switched on, pump (P) starts to work, valves (V1) and (V2) open, tap water enters the anodic tube after passing

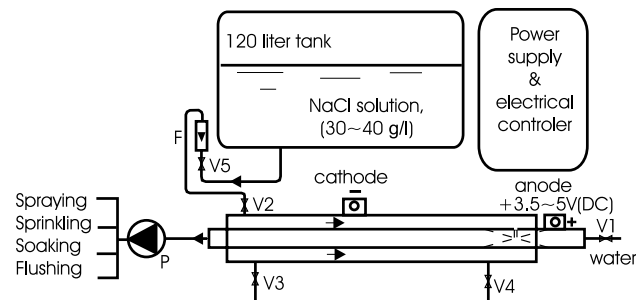


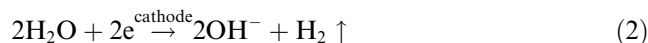
Fig. 1. Schematic diagram of the system set-up.

through a 32-mesh stainless steel net. A high-speed flow velocity of the water at the *Venturi tube* creates a negative pressure (vacuum) in the gap between two concentric electrode tubes. This sucks the dilute NaCl solution (40 g/l) into the gap between two concentric tubular electrodes, the electrolytic cell. More details are shown in Fig. 2.

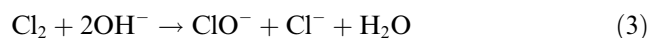
In the electrolytic cell, sodium chloride (NaCl) is electrolyzed immediately to produce an alkaline electrolyte containing chlorine gas and hydrogen gas (Horwood, 1980). Driven by the vacuum, the electrolyte then enters the central stream of the anodic tube and mixes with the bulk water to produce sterilizing water. The electrochemical reactions are illustrated below. On the anode surface the chlorine ions (Cl^-) lose electrons and form the chlorine gas (Bashtan et al., 1999; Horwood, 1980)



On the cathode surface the water molecules gain electrons and form hydrogen gas



The formation of hydroxyl ions alkalinizes the local solution in the vicinity of the cathode surface. In the alkaline environment, the chlorine gas and hydroxyl ions will have a secondary reaction to produce hypochlorous radicals



Hypochlorous radicals (ClO^-) are the main effective component which gives the disinfection action and causes sterilization. The biocidal mechanism of ClO^- is the same as that of the chlorine gas (Cl_2), but the on site production of sodium hypochlorite is a much safer operation.

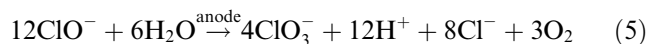
Eqs. (1)–(3) must be balanced, Eq. (1) + (3), gives:



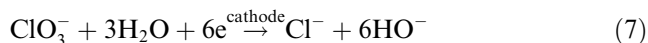
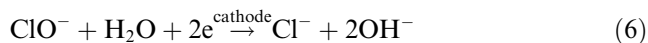
Eq. (3a) indicates that to produce one ClO^- radical, two electrons are required. The water running in the anodic tube is important for cooling the electrolytic cell, since the production of NaClO produces heat as well. When the temperature is higher than 75 °C, some sub-reactions will take place to reduce the electric current efficiency. These unwanted reactions include a divergent reaction, which produces Cl^- and ClO_3^- at the expense of ClO^- . However, ClO_3^- has less efficacy in disinfection and sterilization than ClO^- .



Moreover ClO^- can further discharge on the anode to produce ClO_3^- as well.



On the other hand, if ClO^- and ClO_3^- migrate to the cathode, some retrograde processes, the chemical reduction from ClO^- , ClO_3^- to Cl^- on the cathode may take place:



and OH^- can be oxidized on the anode to release oxygen



Through the newborn ClO_3^- and oxygen are strong oxidants, their biocidal efficacy is much less than that of hypochlorite. Therefore, reactions from (4)–(8) are all unwanted and should be eliminated. For this reason, in the current study, two factors should be considered.

- Keeping the reactor temperature as low as possible, e.g. under 25 °C. This was done by the water flowing in the anodic tube. The temperature of the normal tap water can meet this requirement. Thus the reaction of Eq. (4) could be effectively eliminated, as would the reaction in Eq. (7).

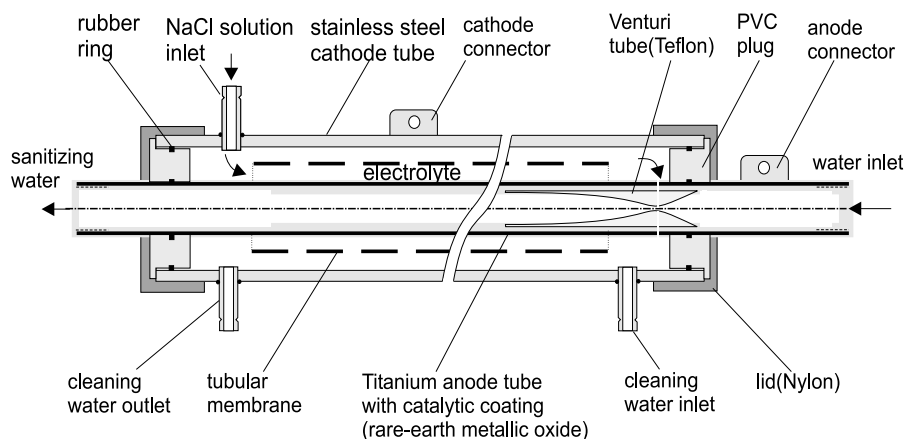


Fig. 2. Schematic diagram of the tubular electrochemical reactor.

- Prevent the chlorine gas (Cl_2) bubbles, which were generated on the anode, from moving towards the cathode surface and contact it. This was done by placing a tubular membrane between the anode and cathode (see Fig. 2).

The membrane used in this study was a standard 16-wire Nylon net (90 μm pores size), which allows the ions to pass through but stops the gas bubbles (the original design is to use an asbestos membrane). Therefore, the reaction expressed in Eqs. (3), (5)–(7) were greatly reduced inside the electrolytic cell consequently. Note that reaction (3) can still take place quickly after the electrolyte was sucked out of the electrolytic cell by the Venturi tube and entered the anode tube, where the chlorine gas (Cl_2) mixed with the cathode liquid rich in hydroxyl ions (OH^-). However reactions (5)–(7) cannot proceed outside the electrolytic cell. Therefore, the electric current efficiency was improved.

Calcium and magnesium ions in the salt solution can form $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ depositing on the cathode so as to reduce efficiency of the electric current. Therefore a purified NaCl solution is preferable, and regular washing with 1% HCl is recommended to remove the deposits.

2.2. Electrochemical reactor

The anatomy of the electrochemical reactor is shown in Fig. 2. The anodic tube was made of titanium (Ti). The dimensions are 38 mm (outer diameter) \times 2 mm (thickness) \times 630 mm (length). This gave an effective electrode area of 500 cm^2 . The outside surface of the titanium tube was coated with a layer of rare-earth metallic oxide, RuO_2 , as the catalytic coating. Here the catalytic layer is critical to reduce the chlorine overpotential in reaction (1) (Horwood, 1980). Without it, the electrolyte process can not proceed economically.

Coating the catalytic layer of RuO_2 is time consuming. The exterior surface of the titanium tube was machined to have fine grid on it (2 \times 2 mm). After being washed and cleaned thoroughly, the titanium tube was defatted with acetone, and submerged in a 90 $^\circ\text{C}$, 10% (w/w) acetic acid solution for 1–2 h to remove its compact oxide layer and produce a microporous structure on its surface. Then the tube was washed in distilled water, and was placed in dehydrated alcohol to protect it from being oxidized again before the coating operation. The coating liquid was prepared in the recipe listed in Table 1 (Horwood, 1980).

This coating liquid was ‘painted’ onto the dried titanium tube surface, then the tube was baked in an oven at 420 $^\circ\text{C}$ for 15 min. This ‘painting-and-baking’ operation was repeated for about 15 times till the coating liquid was used up. In the last baking operation, the oven temperature was set to 450 $^\circ\text{C}$ and the baking time

Table 1
Chemical recipe of the coating material

RuCl_3	36% HCl	<i>n</i> -butanol	<i>Iso</i> -propanol	$\text{Ti}(\text{OC}_4\text{H}_9)_4$	Ti:Ru
1 g	0.5 ml	17 ml	10 ml	3 ml	1:3.46

was prolonged to 1 h to complete the dissolution of RuCl_3 and $\text{Ti}(\text{OC}_4\text{H}_9)_4$, and harden the RuO_2 – TiO_2 layer.

The cathodic tube was made of stainless steel (type 304), which formed a jacket on the outside the anodic tube. It had dimensions of 60 mm (outer diameter) \times 5 mm (thickness) \times 500 mm (length), and an effective electrode surface area of 660 cm^2 . Both ends of the cathodic tube were machined to have screw threads for sealing.

There were some reports and patents dealing with the catalytic layer coating technique on the cathodic surface. For instance, a Chinese Patent (CN 86104356A, 1986) described a cathodic coating for electrolyzing salt water. The preparation was similar to the anodic coating in the aspect of recipe and operation. It claimed to be able to improve the cathodic reaction in Eq. (2) so benefiting electrolysis of the NaCl solution by saving on electricity consumption. However, in this study, the stainless steel cathodic surface was not coated with such a catalytic layer.

The gap between electrodes surface was 6 mm, and the thickness of the membrane, which was a standard #16-wire Nylon net, was about 0.6 mm. The tubular membrane was supported by another porous tube and fixed in an appropriate co-axial position with the electrodes.

2.3. Power supply and control unit

The voltage applied to the electrodes in this study was 3.8–5 V (DC). The current density of the electrode was 0.3 A/ cm^2 . The capacity of the DC power supply was 0.8 kVA. The pump (P) and valves (V1, V2, V3) were operated by the electrical control unit.

2.4. Salt water tank and NaCl solution

The salt-water tank located on a higher level to supply salt water for the electrochemical reactor. Its volume was about 120 l. The tank was made of PVC plastic, which was framed properly with metal material. The NaCl used in this study was the domestic salt available in supermarket. The solution concentration was 40 g/l. Its purity is not ideal for electrolysis. Pre-alkalizing the NaCl solution to pH 9–10 to deposit the $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ in the tank is helpful to put-off mineral fouling happen on the cathode surface. Acid rinsing (1% HCl) of the electrolytic cell is recommended for very 10 h operation.

2.5. Flow control

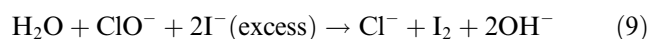
The flow rate of salt water was monitored by a rotameter (F). It can be adjusted manually by valve (V5) according to the requirement of the available chlorine concentration of the output. The flow rate of salt water ranged from 5 to 15 ml/s. The flow rate of the output sterilizing water is controlled using valve V1.

3. Experimental results and discussion

The trial run of the sodium hypochlorite generator was carried out for one season in the crushing house of a cane sugar factory in this study, where the raw sugar canes are crushed, squeezed and soaked with warm water to extract the cane juice. Before the treatment of heating and clarification, this warmed cane juice contains large amount of microorganism. Their number increase exponentially in short time in expense of sucrose and produce unwanted viscous pectin, which increases the difficulty for the subsequent clarification and finally inhibit the sucrose crystallization. The purpose of CIP and SIP is to control the growth of microorganism in the extracted cane juice and reduce the microbial loss of sucrose. The performance of the sodium hypochlorite generator in this trial run is discussed in the following.

3.1. Measurement of available chlorine (ACH)

The concentration of ACH in the output sterilizing water was measured using chemical titration (Fritz & Schenk, 1987). An excess of potassium iodide solution is added to a 100 ml sample of output sterilizing water. The oxidizing chemical, ClO^- , is reduced by the potassium iodide, resulting in the formation of an equivalent amount of iodine, which is titrated with the standard solution of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$. The general scheme is summarized as follows:



The iodine formed in the first reaction (9) is equivalent to the amount of oxidizing agent, ClO^- , in the sample. In this reaction, the iodide (added as potassium iodide) is in large excess (and is not a standard solution). The iodine formed is then titrated with a standard solution of sodium thiosulfate [0.1M], and iodide and tetrathionate ions are formed as the products. Starch is the indicator in this titration. The disappearance of the blue starch–iodine complex marks the end point.

The concentration of ACH in the output sterilizing water can be calculated from the following formula (see derivations in Appendix A)

$$C_{\text{ACH}} = 35.5V_{\text{T}} \text{ (ppm)}, \quad (11)$$

where C_{ACH} is the available chlorine concentration in the liquid, mg Cl_2 per litre (\approx ppm); V_{T} is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ standard solution consumed by titration (ml).

3.2. Salt concentration and electric current efficiency

The working conditions for the sodium hypochlorite continuous generator were selected based on the results of a group of experiments conducted on a small, batch electrolytic cell without a membrane. It was found that the salt concentration in the electrolyte influences the current efficiency. The efficacy of the membrane in a batch electric cell is much less than that in the continuous one. The function of the membrane is to stop the Cl_2 from reacting with OH^- straight away, but if so, the Cl_2 will escape from the liquid to the air. This, in turn, reduces the electric current efficiency. The current efficiency of the electrolytic cell (η_c) is defined as the ratio of experimental chlorine production to theoretical chlorine production when a certain amount of electricity is consumed

$$\eta_c = \frac{\text{measured ACH concentration}}{\text{theoretical ACH concentration}} \times 100\%. \quad (12)$$

Fig. 3 shows the influence of salt concentration on the electric current efficiency. As we can see that the electric current efficiency increases as the salt concentration increases. However, the percentage of salt utilization, on the other hand, decreases as the salt concentration increases. This is shown in Fig. 4. The sodium chloride consumption for producing 1 kg of chlorine, ψ_s , is another parameter of interest, and is also shown in Fig. 4. In this way, an appropriate salt concentration may be chosen on the economical principle.

For temperature, it was found that the lower the better, because low temperature eases Cl_2 dissolving and reduces the rate of sub-reactions (Eqs. (4)–(8)). This

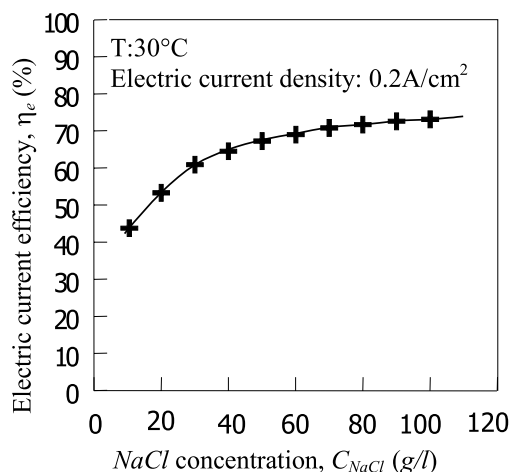


Fig. 3. Salt concentration versus electric current efficiency in a batch electrolytic cell without a membrane between the electrodes.

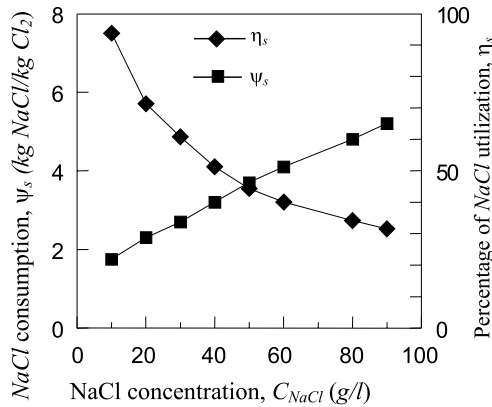


Fig. 4. Salt consumption and utilization percentage variation with the salt concentration in a batch electrolytic cell without a membrane between the electrodes.

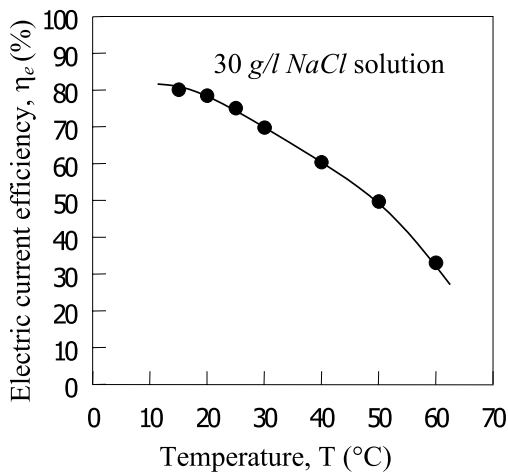


Fig. 5. Electric current efficiency variation with temperature in a batch electrolytic cell without a membrane between the electrodes.

is reflected in Fig. 5. This group of experiments has provided useful criteria for determining the working conditions of the continuous sodium hypochlorite generator. These working conditions are listed in Table 2.

3.3. Influence of bulk water flow rate and the current strength

Eq. (1) shows that to form one molecule of Cl_2 consumes two electrons. Thus according to the Faraday Law, the number of moles of Cl_2 produced is proportional to the quantity of electric charge consumed

$$Q = 2Fn_{Cl_2}, \quad (13)$$

Table 2
Some basic parameters of the electrolytic cell

NaCl concentration (g/l)	NaCl flow rate (ml/s)	Electrolytic voltage (V (DC))	Current density at anode (A/cm ²)	Electrolytic current (A)	Temperature (°C)
30–40	3–5 ^a	3.8–5	0.3	130–150	< 30

^aThis parameter is determined by the following part of analysis.

where Q is the quantity of electric charge (Coulomb) consumed by the electrolytic cell. n_{Cl_2} is the number of moles of chlorine (Cl_2) produced by electrolysis, F the Faraday constant which is 96485.3 C/mol of electrons. The number of moles of chlorine can be expressed as

$$n_{Cl_2} = \frac{m_{Cl_2}}{2 \times 35.5}, \quad (14)$$

where m_{Cl_2} is the mass (gram) of Cl_2 produced in the electrolytic cell. Substituting (14) into (13) gives

$$Q = \frac{F}{35.5} m_{Cl_2} \text{ (C)}. \quad (15)$$

Differentiate Eq. (15) with respect to time (t):

$$I = \frac{dQ}{dt} = \frac{F}{35.5} \frac{dm_{Cl_2}}{dt}, \text{ (C/s, i.e. A)} \quad (16)$$

or

$$\frac{dm_{Cl_2}}{dt} = \frac{35.5}{F} I \text{ (g } Cl_2/s). \quad (16a)$$

However, in producing Cl_2 , the electric current efficiency (η_e) would never be 100% (Fig. 4). Taking the electric current efficiency into consideration, Eq. (16a) should further be modified as

$$\frac{dm_{Cl_2}}{dt} = \frac{35.5}{F} \eta_e I \text{ (g } Cl_2/s). \quad (16b)$$

If the flow rate of bulk water is V_B (ml/s), and the concentration of ACH in the liquid is expressed in ppm (\approx mg/l), then the relationship between ACH concentration, flow rate and electric current strength can be expressed as

$$\begin{aligned} C_{ACH} &= \frac{1000 \times (dm_{Cl_2}/dt)}{(V_B/1000)} = \frac{3.55 \times 10^7 \eta_e I}{F V_B} \\ &= 367.88 \frac{\eta_e I}{V_B} \text{ (ppm)}. \end{aligned} \quad (17)$$

In this study, the capacity of the DC power supply was 0.8 kVA. The recommended electrode current strength was 150 A working at a voltage of 4 V (DC).

Fig. 6 shows some typical experimental results conducted in the continuous sodium hypochlorite generator. The solid lines of it are the theoretical values of the ACH concentration. That the measured ACH concentration was smaller than the theoretical values implies that the electric current efficiency was lower than 100%. The average value of current efficiency η_e under the condition of 150 A electric current strength, 20 °C and 40 g/l salt concentration, was about 82%, it slightly in-

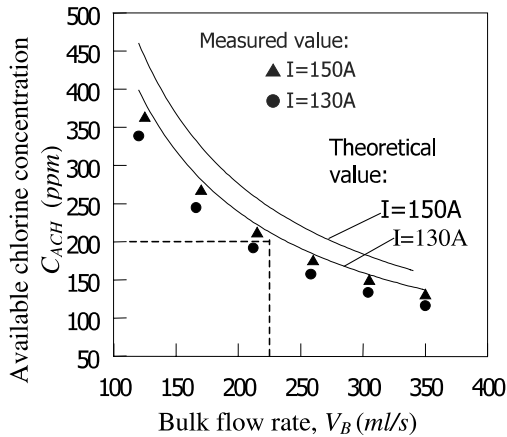


Fig. 6. The ACH concentration in output flow varies with the flow rate and the electrode current strength under the condition of 20 °C and 40 g/l salt concentration in the electrolytic cell.

creased to 85% when the electric current strength was reduced to 130 A.

3.4. Salt water flow rate

The flow of salt water via the rotameter (F) into the electrolytic cell replenished the NaCl which was electrolyzed to produce NaClO. Combining Eqs. (1) and (2) to give a full reaction:



According to Eq. (1a), theoretically, to produce 1 kg of chlorine gas (Cl_2) requires 1.648 kg of sodium chloride (NaCl). Since the percentage of salt utilization (η_s) would never be 100%, if take the η_s into consideration, we will have

$$\eta_s m_{\text{NaCl}} = 1.648 m_{\text{Cl}_2}, \quad (18)$$

where m_{NaCl} is the mass of NaCl consumed; m_{Cl_2} , the mass of Cl_2 produced. As mentioned before, the ratio of m_{NaCl} to m_{Cl_2} , namely, the salt consumption for producing 1 kg of chlorine, ψ_s , is also important. ψ_s and η_s are related by Eq. (18a). This relation is also indirectly reflected in Fig. 4.

$$\psi_s \eta_s = 1.648. \quad (18a)$$

Differentiate Eq. (18) against time (t) to give

$$\eta_s \frac{dm_{\text{NaCl}}}{dt} = 1.648 \frac{dm_{\text{Cl}_2}}{dt}. \quad (19)$$

Converting the mass flow rate, (dm_{NaCl}/dt), into volume flow rate, (V_{NaCl} , ml/s), which can be measured with the rotameter (F), gives

$$\frac{dm_{\text{NaCl}}}{dt} = \frac{C_{\text{NaCl}} V_{\text{NaCl}}}{1000} \quad (\text{g/s}), \quad (20)$$

where C_{NaCl} is the salt concentration (g/l) of salt water in the tank. Substitute Eqs. (20) and (16b) into (19) and re-arrange it to give:

$$\eta_s C_{\text{NaCl}} V_{\text{NaCl}} = \frac{1000 \times 1.648 \times 35.5}{F} \eta_e I \quad (21)$$

or

$$\eta_s C_{\text{NaCl}} V_{\text{NaCl}} = 0.6063 \eta_e I. \quad (22)$$

To replenish the NaCl in the electrolytic cell, a certain flow rate of salt water, V_{NaCl} (ml/s), which has a salt concentration of C_{NaCl} (g/l) should be sustained. In the electrolytic cell, if the current strength is I (A), the electric current efficiency is η_e , and the percentage of salt utilization is η_s , the balance of supply and demand of NaCl in the electrolytic cell is fully described by Eq. (22). For instance, the typical values of $I\eta_s$, η_e , and C_{NaCl} are 150 A, 80%, 60% and 40 g/l, respectively, thus the salt-water flow rate should be adjusted to the value of

$$V_{\text{NaCl}} = \frac{0.6063 \times 80\% \times 150}{60\% \times 40} = 3.03 \quad (\text{ml/s}). \quad (23)$$

It is the reason that the salt-water flow rate was set to 3–5 ml/s in this study. A higher flow rate of salt water was found to give a higher ACH concentration in this study, because the dynamic concentration of NaCl was increased by a exceeding supply of NaCl in the electrolytic cell, which increased the electric current efficiency.

At this flow rate of salt-water, the 120-l tank of salt water can sustain continuous work for more than 9 h, and produce about 7200 l of sodium hypochlorite solution. The available chlorine concentration is 200 ppm in the bulk water flow rate of 225 ml/s, i.e., 810 l/h and the electrode current of 130 A. These can be found in Fig. 6.

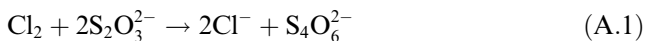
4. Summary

The NaClO continuous generator studied was a pilot scale equipment used for anti-microbial for CIP and SIP in the food industry. The electrolytic cell was constructed as a tubular electrochemical reactor, with a nylon net membrane between the anode and cathode. Its capacity was 0.8 kVA. The available chlorine production rate is determined by the electrode current strength. When the concentration of the salt water in the electrolytic cell was 40 g/l, and its flow rate was 3.6–5 ml/s, and the electrolytic current was about 150 A under 3.5 V (DC) electrode voltage at 20 °C, the output sterilizing water would have an available chlorine concentration of 200 ppm at a flow rate of 250 ml/s. The electric current efficiency was 81%. The utilization percentage of NaCl is about 60%, which means the sodium chlorine consumption was 2.7 kg to produce 1 kg available chlorine (Cl_2). A salt-water tank of 120 l can sustain a continuous work for about 9 h, and produces 7200 l of sterilizing water at the available chlorine concentration of 200 ppm.

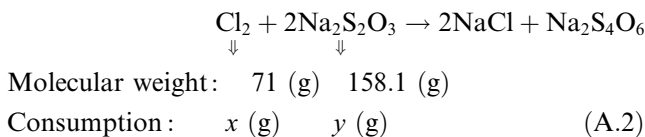
Appendix A

Derivations of Eq. (11) for calculating the ACH concentration by titration.

Note Eqs. (9), (10) and (3) must be balanced, giving:



or written as



So

$$x = \frac{71}{2 \times 158.1} y. \quad (\text{A.3})$$

Assume that the consumption of the standard solution of sodium thiosulfate (0.1 mol l^{-1}) is V_T (ml), thus the weight of $\text{Na}_2\text{S}_2\text{O}_3$ consumed would be

$$\begin{aligned} y &= \frac{0.1 \times 158.1 \times V_T}{1000} \\ &= \frac{158.1 V_T}{10,000} \text{ (g Na}_2\text{S}_2\text{O}_3 \text{ per 100 ml liquid)} \end{aligned} \quad (\text{A.4})$$

Substituting Eq. (A.4) into Eq. (A.3), gives:

$$x = \frac{35.5}{10000} V_T \text{ (g Cl}_2 \text{ per 100 ml liquid)} \quad (\text{A.5})$$

Converting x to the unit of mg/l (i.e. ppm), gives

$$C_{\text{ACH}} = \frac{35.5 V_T}{10,000} \times 10 \times 1000 = 35.5 V_T \text{ (ppm)}, \quad (\text{A.6})$$

where C_{ACH} is the available chlorine concentration in the liquid ($\text{mg Cl}_2/\text{l}$, \approx ppm). V_T is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ standard solution consumed by titration (ml).

References

- Abd el Meguid, E. A., Mahmoud, N. A., & Gouda, V. K. (1998). Pitting corrosion behaviour of AISI 316L steel in chloride containing solutions. *British Corrosion Journal*, 33(1), 42–48.
- ATUO Chemical Ltd. (1986). The Fabrication of a cathode used for electrolysis. Chinese Patent. CN 86104356A (Chinese).
- Bashtan, S. Y., Goncharuk, V. V., Chebotareva, R. D., Belyakov, V. N., & Linkov, V. M. (1999). Production of sodium hypochlorite in an electrolyser equipped with a ceramic membrane. *Desalination*, 126(1–3), 77–82.
- Behrsing, J., Winkler, S., Franz, P., & Premier, R. (2000). Efficacy of chlorine for inactivation of *Escherichia coli* on vegetables. *Post-harvest Biology and Technology*, 19, 187–192.
- Borovec, S., Broumis, C., Adcock, W., Fang, R., & Uren, E. (1998). Inactivation kinetics of model and relevant blood-borne viruses by treatment with sodium hydroxide and heat. *Biologicals*, 26(3), 237–244.
- Craig, B. D., & Anderson, D. S. (Eds.). (1995). *Materials data series, Handbook of corrosion data*. Metals Park, OH: ASM International.
- Dodds, M. G., Grobe, K. J., & Stewart, P. S. (2000). Modeling biofilm antimicrobial resistance. *Biotechnology and Bioengineering*, 68(4), 456–465.
- Eginton, P., Holah, J., Allison, D., Handley, P., & Gilbert, P. (1998). Changes in the strength of attachment of micro-organisms to surfaces following treatment with disinfectants and cleansing agents. *Letters in Applied Microbiology*, 27(2), 101–105.
- Flint, S. H., van den Elzen, H., Brooks, J. D., & Bremer, P. J. (1999). Removal and inactivation of thermo-resistant streptococci colonising stainless steel. *International Dairy Journal*, 9(7), 429–436.
- Fritz, J. S., & Schenk, G. H. (1987). *Quantitative analytical chemistry*. INC: Boston Allyn and Bacon.
- Horwood, E. (1980). *Modern chlor-alkali technology*. New York: Society of Chemical Industry (Great Britain).
- Hua, F., West, J. R., Barker, R. A., & Forster, C. F. (1999). Modeling of chlorine decay in municipal water supplies. *Water Research*, 33(12), 2735–2746.
- Joseph, B., Otta, S. K., Karunasagar, I., & Karunasagar, I. (2001). Biofilm formation by *Salmonella* spp. on food contact surfaces and their sensitivity to sanitizers. *International Journal of Food Microbiology*, 64, 367–372.
- Laycock, N. J., Stewart, J., & Newman, R. C. (1997). The initiation of crevice corrosion in stainless steels. *Corrosion Science*, 39(10–11), 1791–1809.
- Neville, A., Hodgkiess, T., & Destriau, X. (1998). Initiation and propagation of localised corrosion on stainless steels in sea-water containing high biocide concentrations. *Corrosion Science*, 40(4–5).
- Prutz, W. A. (1999). Consecutive halogen transfer between various functional groups induced by reaction of hypohalous acids: NADH oxidation by halogenated amide groups. *Archives of Biochemistry and Biophysics*, 371(1), 107–114.
- Racioppi, F., Daskaleros, P. A., Besbelli, N., Borges, A., Deraemaecker, C., Magalini, S. I., Martinez, A. R., Pulce, C., Ruggerone, M. L., & Vlachos, P. (1994). Household bleaches based on sodium hypochlorite review of acute toxicology and poison control center experience. *Food and Chemical Toxicology*, 32(9), 845–861.
- Reinemann, D. J. P., R.W., & Mein, G. A. (1997). Control strategies for milking parlor clean-in-place systems. *Transactions of the ASAE*, 40(6), 1749–1752.
- Rossoni, E. M. M., & Gaylarde, C. C. (2000). Comparison of sodium hypochlorite and peracetic acid as sanitising agents for stainless steel food processing surfaces using epifluorescence microscopy. *International Journal of Food Microbiology*, 61, 81–85.
- Soriano, J. M., Rico, H., Molto, J. C., & Manes, J. (2000). Assessment of the microbiological quality and wash treatments of lettuce served in University restaurants. *International Journal of Food Microbiology*, 58, 123–128.
- Tauxe, R., Hedberg, C., Potter, M., Madden, J., & Wachsmuch, K. (1997). Microbial hazards and emerging issues associated with produce. A preliminary report to the National Advisory Committee on microbiologic criteria for foods. *Journal of Food Protection*, 60, 1400–1408.
- Tournas, V. (1994). Heat-resistant fungi of importance to the food and beverage industry. *Critical Reviews in Microbiology*, 20(4), 243–263.
- Weissinger, W. R., Chantarapanont, W., & Beuchat, L. R. (2000). Survival and growth of *Salmonella* baillon in shredded lettuce and diced tomatoes, and effectiveness of chlorinated water as a sanitizer. *International Journal of Food Microbiology*, 62, 123–131.