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Design of a Tank Electrolyser for In-situ Generation of NaClO

K.Asokan and K.Subramanian

***Abstract*— Sodium hypochlorite (NaClO) is used on a large scale for surface purification, fabric bleaching, odour removal and water disinfection. It has numerous advantages namely simple dosage, safe storage and transportation and leaves no residual effluent. Electro synthesis of NaClO is preferred due to the environmental hazard associated with the storage and transportation of liquid chlorine. It is now becoming popular for users to produce their own hypochlorite solutions by means of undivided electrolytic cells by direct electrolysis of weak brine or seawater. These cells can be designed for any desired production capacity. Design of a simple tank electrolyser for the in - situ generation of NaClO is presented**

***Index Terms*— in-situ generation, undivided cell, sodium hypochlorite.**

I. Introduction

Sodium hypochlorite (NaClO) is used on a large scale for surface purification, fabric bleaching, odour removal and water disinfection [1]-[3]. In-situ produced hypochlorite was used for anodic oxidation of dye molecules [4]-[8] and phenols [9] in the wastewater. As a bleach and disinfectant it has numerous advantages namely simple dosage, safe storage and transportation and leaves no residual effluent. In household (5%) bleach form, sodium hypochlorite is used for the removal of stains from clothes. Post-treatment with weak organic acids such as acetic acid (vinegar) will neutralize the NaOH, and volatilize the chlorine from residual hypochlorite. A 1 in 5 dilution of household bleach is effective against most of the bacteria and viruses. It is often the disinfectant of choice in cleaning surfaces in hospitals. Sodium hypochlorite has been used for the disinfection of drinking water. About 1 liter of household bleach disinfects 4000 liters of water. Sodium hypochlorite has been used to destroy cyanide wastes. Sodium hypochlorite is applied in swimming pools for water disinfection. It has the advantage that microorganisms cannot build up any resistance to it.

Most of the hypochlorite solutions sold contains 3 - 5 % of sodium hypochlorite at the time of manufacture; strength gradually decreases on storage. The stability of sodium hypochlorite solutions will be more if they are of low concentration; solution pH is 11.5 - 13; graphite particles and metallic ions are absent; temperature is around 303 K and the containers are impermeable to light. Electro synthesis of NaClO is preferred due to the environmental hazard associated with the storage and transportation of liquid chlorine. It is now becoming popular for users to produce their own hypochlorite solutions by means of undivided electrolytic cells by direct electrolysis of weak brine or seawater. These cells can be designed for any desired production capacity. Design of a simple tank electrolyser for the in - situ generation of NaClO is presented in this paper.

II. Principle and Methodology

NaClO is electrochemically produced by electrolyzing synthetic sea water (aqueous 3% NaCl solution) or sea water in an undivided electrolytic cell using Noble metal oxide coated Titanium anode and Steel or Titanium cathode . Electrolyte is pumped to a constant level tank, from where it is fed to the bottom of the tank type electrolyser, made of PVC. Feeding of sodium chloride brine from the constant level tank ensures uniformity in cell feed rate. Electrolysis leads to the generation of chlorine at the anode and caustic at the cathode. Chemical reaction between the chlorine gas and caustic solution results in the in - situ generation of NaClO.

At anode:

$$NaCl \rightarrow Na^+ + Cl^- ; \quad 2Cl^- - 2e^- \rightarrow Cl_2 \qquad (1).$$

At cathode:

$$H_2O \rightarrow H^+ + OH^-;$$

$$2H^+ + 2e^- \rightarrow H_2 ; \quad Na^+ + OH^- \rightarrow NaOH \qquad (2)$$

In the tank::

$$NaOH + Cl_2 \rightarrow NaClO + NaCl + H_2O. \qquad (3)$$

NaClO solution is withdrawn from the top of the electrolyser at the end opposite to that of the feeding point. The process flow sheet for the *in–situ* generation of NaClO is given in Fig.1. The electrode assembly is shown in Fig.2. Fig 3 shows the position of electrode assembly in the tank.

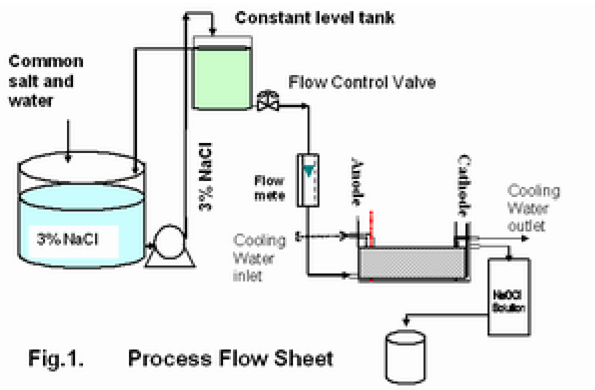

Fig.1. Process Flow Sheet

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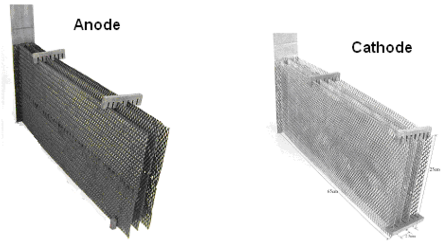

Fig.2. Electrode Assembly

Fig. 3. Electrode Assembly fitted in the Tank

III. Design of Tank Electrolyser for In-situ Generation of NaClO

1. Selection of electrode materials:

Success of an electrochemical technology depends on the proper selection of electrode material. A good electrode material should have good electro catalytic activity and selectivity to ensure the required rate of formation and purity of the end product; should have excellent stability under open circuit conditions: should also be readily available at reasonable cost. Usually the choice is based on a compromise between activity, selectivity and cost. An excellent electro catalyst with low chemical stability will be technologically less interesting than a material with lower electro catalytic properties but of much better stability.

Anode:

The anodic reaction in the case of electrolytic generation of NaClO is chlorine evolution. The best anode material for this is noble metal oxide coated titanium expanded mesh, where, chlorine evolution reaction occurs with low overpotential at high current efficiency. Electrodes have very good chemical stability in the electrolyte. In general, expanded mesh configuration is the best for gas evolution reactions to disengage the gas bubbles as and when they are formed on the electrode surface.

Cathode:

On the other hand, cathode material may be mild steel or titanium mesh. But mild stable is not stable under open circuit conditions in weak brine. Mild steel corrodes and contaminates the electrolyte and the final product. Titanium is the best cathode material. Cathodic reaction is hydrogen evolution along with hydroxide ion generation; hydroxide ions combine with the calcium and magnesium ions present in raw water and commercial sodium chloride leading to the precipitation of their hydroxides [10]-[14]. It builds up a thin scale on the cathode surface that increases resistance and cell voltage. The scale can easily removed by periodically flushing of the electrolyser with dilute hydrochloric acid solution.

2. Optimisation of process parameters:

To optimize the process parameters for the commercial scale electrolyser, a lab scale electrolyser was designed and fabricated using PVC as material of construction.

Three number coated titanium mesh of size 16 cm × 6 cm tag welded together formed the anode assembly. Four number uncoated titanium mesh or mild steel form of size 16 cm × 6 cm tag welded together formed the cathode assembly. The anode assembly is kept inside the cathode assembly in such a way the distance between adjacent anode and cathode is constant at 1 cm using suitable PVC spacers. The electrode assembly as a whole is positioned at the geometric centre of the cell tank. Experiments were conducted to fix, the optimum current density, electrolyte flow rate, operating cell temperature and hold up or volume current concentration. Based on the results of the optimization studies, the Lab scale electrolyser was scaled up to the commercial size.

The electrolyte is an aqueous solution of 30g.L^{-1} commercial sodium chloride in raw water. The electrolyte is fed at the bottom and the effluents taken out at the top of the electrolyser. The flow of the electrolyte is continuous. The NaClO produced is estimated by volumetric analysis using iodimetric technique. To study the effect of a parameter process parameter, all the other parameters except that parameter are kept constant.

Optimum current density:

In electro chemical reactions, production is based on quantity of current passed, as per faraday's first law of electrolysis. In Industry, current passed is usually reported in terms of current density which denotes the current passed per unit electrode area. As current density is increased, hypochlorite production also increases [15],[16]. But cell temperature also increases with increase in current density. Above a temperature 308 K, sodium hypochlorite tends to chemically decompose to sodium chlorate.

$$3NaClO \rightarrow NaClO_3 + 2\ NaCl \qquad (4)$$

So when temperature goes above 308 K, production of NaClO falls. Fig.4 shows that the concentration of NaClO increases up to 50 mA.cm^{-2}, but at higher current densities the concentration decreases due to increase in temperature. In other words, rate of decomposition of hypochlorite increases with increase in current density. Optimum current density is 50 mA.cm^{-2}, at which the maximum concentration of hypochlorite is obtained.

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Fig 4

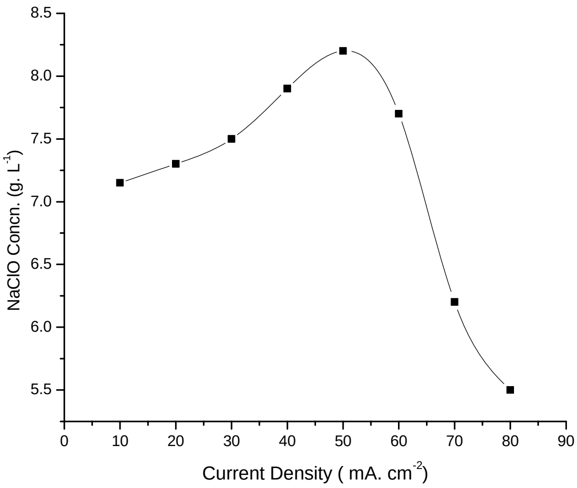

Fig 4. Effect of current density on NaClO concentration.
Feed : 30 g L-1 NaCl; Flow rate: 3.6 L h-1; Anode : TSIA ; Cathode: Ti, Electrolyser volume: 25 L ; Electrolysis Time: 1 hour; Temperature : 308 K

Optimum flow rate:

The flow rate is inversely related to the NaClO concentration and directly related to the current efficiency. Increase in flow rate decreases the rate of decomposition reaction but at the same time decreases the NaClO concentration. Fig.5 shows the effect of flow rate on Hypo concentration obtainable for electrolytic hypo generation. Optimum flow rate is 3.6 L h^{-1}, at which the maximum concentration of the hypochlorite is obtained at a reasonable current efficiency.

Fig.5

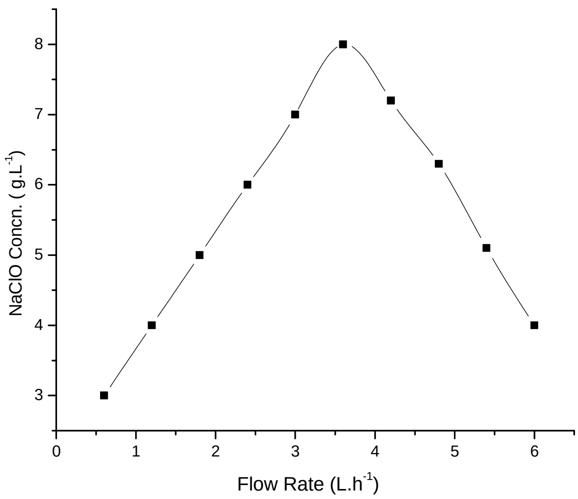

Fig.5. Effect of flow rate on NaClO built up Concentration.
Feed : 30 gL-1 NaCl; Current Density: 50 mA. cm^{-2}; Anode : TSIA; Cathode: Ti Electrolyser volume: 25 L ; Electrolysis Time: 1 hour; Temperature : 303 K

Optimum operating temperature:

Temperature plays a vital role in the electro generation of hypochlorite. Increase of temperature decreases NaClO concentration and current efficiency of the reaction. Low temperature favours the higher NaClO generation. Higher temperature leads to chemical decomposition of the hypo formed as mentioned already. The electrolyser has to be maintained at the ambient temperature at which a maximum NaClO concentration of about 8 g. L^{-1} is produced.

Fig.6

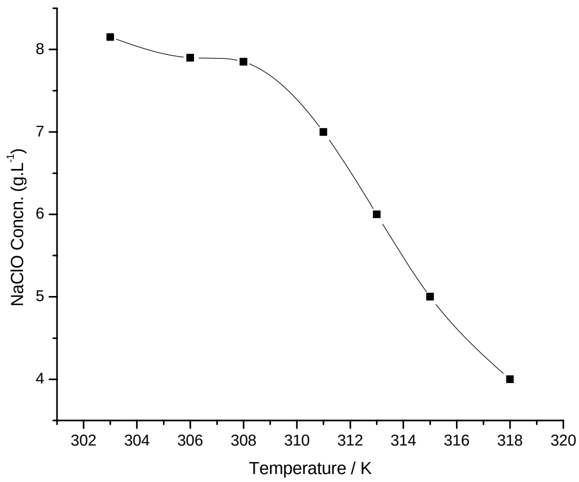

Fig.6. Effect of temperature on NaClO built up Concentration.
Feed : 30 g.L-1 NaCl; Flow rate: 3.6 L h-1; Current Density: 50 mA cm^{-2}; Anode : TSIA ;Cathode: Ti; Electrolyser volume: 25 L ;Electrolysis Time: 1 hour

Optimum holdup Volume:

Electro generation of sodium hypochlorite is an electro chemical process followed by a chemical process; both take place in the same vessel. While the electrochemical process is instantaneous, the chemical process is not so. It requires a definite time for effective contact between the reactant species, namely NaOH and Cl_2. Volume of the vessel is a measure of the residence time. To fix the optimum residence time, the process is carried out in different electrolyser tanks of volume ranging from 15 L to 45 L. Production from each of the tank is monitored. The production from the 25 L capacity tank the maximum, indicating that 25 L is the optimum hold up volume for the process conditions we have adopted for the present studies.

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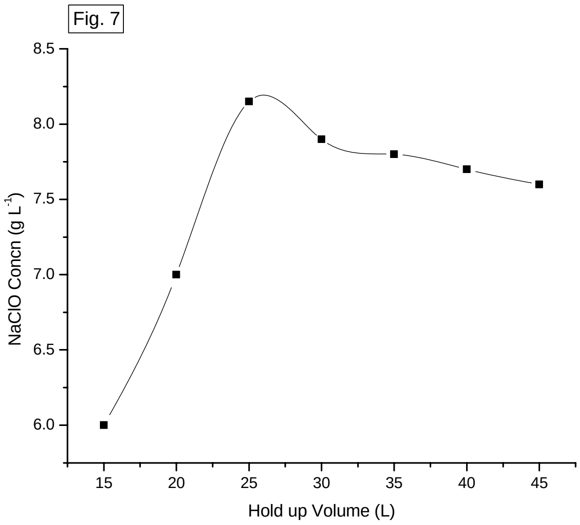

Fig.7. Effect of hold up volume on NaClO built up Concentration.
Feed : 30 g .L-1 NaCl ; Flow rate: 3.6 $L.h^{-1}$; Current Density: 50 mA. cm^{-2}, Anode : TSIA; Cathode: Ti; Electrolysis Time: 1 hour; Electrolysis continued until to reach steady state NaClO concn. (2-3 hours)

The studies present the following optimum process parameters for NaClO production .

Current Density	: 50 mA cm^{-2}.
Cathode Material	: Titanium
Holdup volume	: 25 litre
Flow Rate	: 3.6 L h^{-1}.
Temperature	: 308 K.

Assuming a safe scale up factor of five, an electrolyser having electrode area five times that of the electrolyser used for optimization studied was designed, fabricated and operated. Operation data is given in Table I

Table I. Typical operating data for the production of 4 – 5 $g.L^{-1}$ NaClO solution

Anode	Coated Ti (TSIA) mesh.
Cathode	Ti expanded Mesh
Separator	Nil.
Anode Area	1500 cm^2 – 3 nos.
Cathode area	1500 cm^2 – 4 nos
Anodic current density	50 mA cm^{-2}
Cell voltage	3.7 – 3.8 V
Current concentration	1.6 A L^{-1}
Electrolyser dimensions	110cm × 35 cm × 30 cm.
Electrolyser volume	125 L.
Brine feed rate	0.15 – 0.2 L AH^{-1}
Cell temperature	300 -303 K.
Strength of NaClO	4 - 5 g L^{-1}
Current efficiency	50 – 60%
Production of NaClO	30 L h^{-1}
Power consumption	5 - 6 kWh kg^{-1} NaClO

Five electrolysers of the above specification designed, fabricated and operated in series will produce 1000 L. h^{-1} of hypo solution per shift of 8 hours. The rectifier rating required for the plant is 250 A;60 V.

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REFERENCES

[1]. Connell, GF.. The chlorination/chloramination handbook. American Water Works Association, Denver, CO, USA. 1996
[2]. USEPA. 1999. Alternative disinfectants and oxidants, guidance manual. EPA 815-R-99-014, April 1999.
[3]. CCC (Chlorine Chemistry Council).. Drinking water chlorination. A review of disinfection practices and issues. 2003, Internet access: http://c3.org (accessed 09-11-2008)
[4]. C.-H. Yangi, C.-C. Lee, T.-C. Wen, *J. Appl.Electrochem*. 30 (2000) 1043-1051,
[5]. D. Rajkumar, J. G.Kim, *J. Hazardous Materials* B136 (2006) 203
[6]. K Scott, Electrochemical process for clean technology, the royal society of chemistry, 1995, p.189.
[7]. D. Pletcher, F. C Walsh. Industrial electrochemistry, Second edition, Chapman and Hall Ltd, 1990.
[8]. C.D. Ellingson, New mater. New processes electrochem. Tech. 1981, 1, 245.
[9]. D.Rajkumar, J.G.Kim. *Chem.Eng.Technol*. 28(2005) 98
[10]. D. W. Kirk and A. E. Ledas**,** *International Journal of Hydrogen Energy*
Volume 7, Issue 12, 1982, Pages 925-932.
[11]. D. Pletcher, F.C. Walsh. *Industrial Electrochemistry,*2nd ed. Chapman and Hall Ltd, 1990
[12]. H. K. Abdel-Aal and I. A. Hussein**,** ***International Journal of Hydrogen Energy***, Volume 18, Issue 7, July 1993, Pages 553-556 ,
[13]. C. Boxall, G.H. Kelsall, I. Chem. E. Symp.``*Electrochemical Engineering and the Environment"*, Vol. 127, 1992, p. 59.
[14]. G.H. Kelsall, I. Chem. E. Symp. *Electrochemical Engineering and the Environment*, Vol. 127, 1992,
[15]. B Cyna, G Dourdin, D Gatel. Modern Chlor-Alkali Technology, Volume 7, 1998, p.197.
[16]. W.A. Koehler, Principles and applications of electrochemistry, volume 2, Second edition, Chapman and Hall ltd, London. 1959, p.282.