

On site Electrochemical Production of Sodium Hypochlorite Disinfectant for a Power Plant utilizing Seawater

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Received: 24 February 2012 / Accepted: 9 April 2012 / Published: 1 May 2012

This investigation deals with the application of electrochemical technology for the onsite generation of sodium hypochlorite (NaOCl) from seawater for utilization in the power industry. The interaction at different levels of several variables namely, the electrode type and their surface area ratio, current density, and inter-electrode spacing were monitored. A laboratory scale reactor having two electrodes was fabricated and implemented to achieve the objective. The highest production of NaOCl was obtained using a titanium electrode coated with a dimensionally stable anode (DSA) that gave high-current efficiency and superior durability. Maximum production was achieved using titanium under conditions of 72.4 mA/cm² current density, 7 cm inter-electrode spacing and a value of 1 for the anode to cathode surface area ratio. Although at higher surface area ratios, more NaOCl production was observed, the increase in its production was marginal for ratios above unity in comparison to ratios below unity. Hence, a ratio of unity was chosen as a practical value which also reduced the costs of the process. This was found to be similar to, if not better than, results reported in the literature. Optimization studies using design of experiments are recommended in the future.

Keywords: Sodium hypochlorite; seawater; disinfection; electrochemical technology; power industry

1. INTRODUCTION

Industries require huge quantities of cooling and/or process water and are generally located near large water bodies such as sea shores. One of the drawbacks in utilizing seawater directly is the

presence of microbiological organisms such as algae and bacteria. High concentration of these organisms has been attributed to the fouling of piping systems at the inlet to the conduit [1, 2].

The formation of this slime causes a reduction in the heat-transfer capacity of the equipment. This is more pronounced in the case of industrial plants that consume large quantities of water; typical of power plants which in addition requires cooling during many stages of the plant's cycle. It is thus, understandably a major concern and a responsibility of power plant engineers and operators to ensure that the cooling water circuits are maintained by reducing bio-fouling which adversely affects the heat-transfer surfaces.

Microbiological fouling in cooling circuits is initiated by biofilms, which are colonies of a variety of bacteria; a slimy substance they produce called exopolysaccharide (EPS) holds it all together. Biofilms also serve as collection sites for silt and other debris that can accumulate on cooling tower fill and lead to structural damage. Biofilms initiate the formation of mineral scales such as magnesium and calcium carbonate. These scales eventually mitigate the flow of cooling water to heat exchanger surfaces, accelerate localized corrosion by limiting oxygen diffusion, and causes disparaging turbulence in the cooling circuit. This can severely damage the equipment and significantly reduce their lifespan [3]. Micro-fouling is caused by bacteria, slime, algae and particulate matter of either biological or inorganic origin. These fouling elements from seawater intake systems deposit on heat exchanger, condenser tubes, tube sheets, and other piping systems. Once this material forms a cladding over the heat-transfer surfaces, it ultimately results in plant downtime associated with unnecessary shutdown and the maintenance and replacement of parts as the case may be. Bio-fouling possibly affects the cooling system performance in various ways. Internal diameter of the heat exchanger or condenser tubes may reduce the intake in pipes. Increase in the cooling circuit resistance ultimately increases the pumping requirements. Significant reduction in the heat-transfer capacity results due to the formation of a biological slime at the outer shell which has a poor thermal conductivity than metal [4, 5].

Generally, disinfecting seawater is a common and economical solution to prevent or minimize biological fouling in the system. The purpose of seawater disinfection is to inactivate biological organisms and retard their growth to minimize the fouling [6]. Of the several disinfection techniques, ozonation, ultra-violet (UV) irradiation and chlorination have been widely reported. However, the latter is the most economical. An even more attractive option is when it is generated in situ [5, 7, 8].

The Hub Power Company (HUBCO) situated about 60 km from Karachi is private-sector power plant in Pakistan. It is a 1200 MW (Megawatt) thermal power plant consisting of four power generating units of 323 MW gross outputs each. The requirement of cooling water for the condensers and auxiliary plant is obtained from the Arabian Sea through a 300 m long submerged concrete inlet channel leading to a silt settling basin. Seawater is conveyed further through an open inlet canal that is about 650 m long to the pump house. The sea water flows from the water intake structure after passing through screens to remove debris and is pumped by the main circulating pumps through the intake piping and valves to the condensers.

At the Hub Power Plant disinfection using chlorine gas was employed to manage the biological growth which generally choked the condenser tubes and ultimately resulted in a drastic decrease in heat transfer capacity and increased the process water temperature. The average requirement of

chlorine in the facility ranged between 545 kg to 625 kg [9]. However, inherent hazards in handling and transporting chlorine which required strict regulatory compliance motivated the management to search for some convenient and onsite disinfection methods [8].

Liquid NaOCl is one of the options to perform a disinfection process. However, high corrosive nature and readily decaying property of NaOCl during storage questioned the suitability as a candidate on its own [10-12]. On-site production of NaOCl is a promising and a more attractive alternative to the chlorination approach as it is safe and effective. Furthermore, the two constituents required for the production (seawater and electricity) are available in sufficient amounts at the HUBCO facility. In the NaOCl production, electrochemical process (EC) is one of the viable options considered because it can provide the disinfectant in desired quantity and quality when and where required [13].

The aim of this paper is to determine practical operating conditions for the electrochemical production of NaOCl from seawater. The effect of the controlling variables namely electrode type, current density, electrodes surface area ratio and inter-electrode spacing were studied.

2. EXPERIMENTAL

A bench scale setup with a length of 250 mm and an outer diameter of 200 mm was fabricated to assess the NaOCl production capability of the prototype cell from seawater.

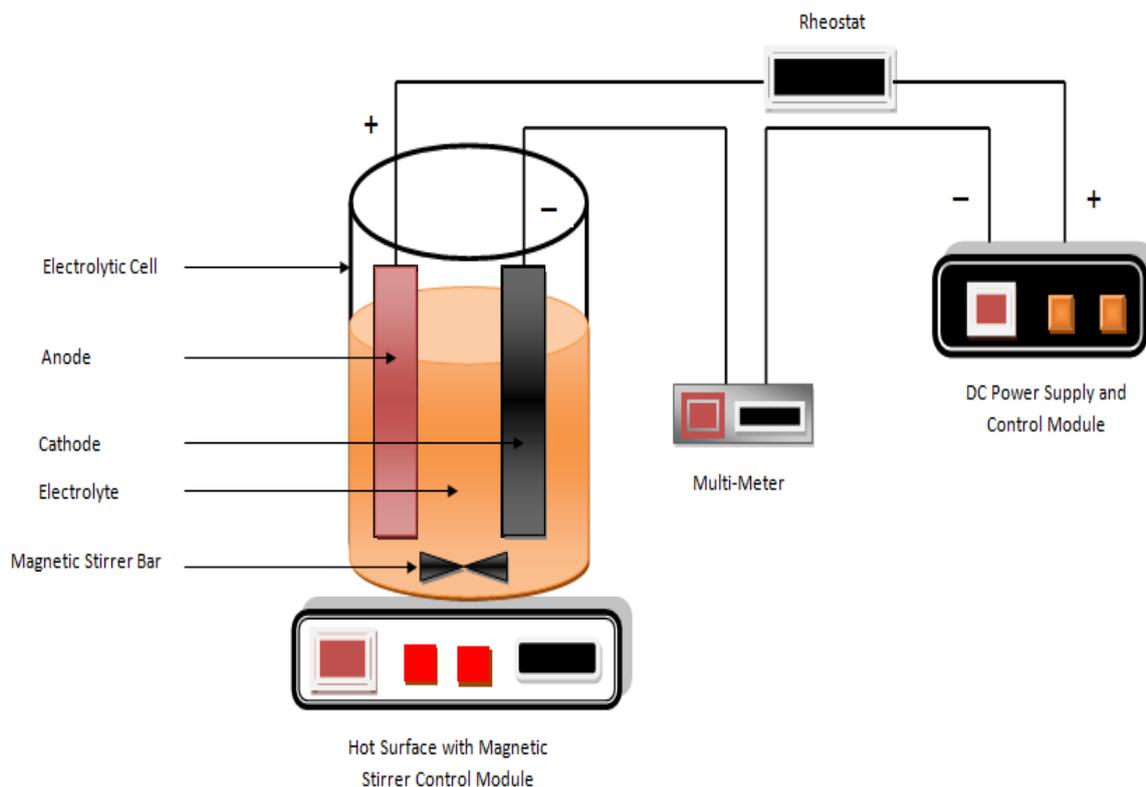


Figure 1. Schematic of sodium hypochlorite production electrochemical set-up (not to scale)

As shown in the schematic sketch (Figure 1) the cylindrical shaped reactor consisted of electrodes each having a dimension of 175 mm × 180 mm and thickness of 2.5 mm. The electrodes were immersed in the seawater and connected to a DC power supply (Matsusada Precision, REK-200-18). For each experimental run, a constant electrode spacing of 15 cm was maintained, unless inter-electrode spacing was the variable of interest.

In each batch experiment 3,000 ml of seawater was utilized while the temperature was maintained between 25 to 26 °C. Each experimental run continued for at least 2.5 h. Seawater samples were collected from the cell every 20 min and transported to the laboratory for NaOCl concentration determination following standard procedures [14]. The physical & chemical characteristics of seawater used in this study are presented in Table 1.

Table 1. Physical and chemical characteristics of seawater

Parameter*	Minimum	Maximum	Mean
Temperature	17	30	27
pH at 25 °C	8.0	8.3	8.1
Turbidity	0	28.5	17.9
Conductivity	--	--	53.0
Total Hardness as CaCO ₃	6,290	7,500	6,900
Total Dissolved Solids (TDS)	35,200	41,000	38,900
Total Solids (TS)	--	--	45,100
Calcium as Ca ²⁺	380	590	520
Magnesium as Mg ²⁺	1,290	1,510	1,400
Sodium as Na ⁺	10,500	15,600	14,500
Potassium as K ⁺	350	490	460
Chloride as Cl ⁻	19,400	25,200	24,500
Sulfate as SO ₄ ²⁻	2,680	3,100	2,800
Oil	--	--	N.D.

*All units are in mg/l except temperature (°C), turbidity (NTU) and conductivity (mS/cm), N.D. = Not detected.

In order to select a candidate electrode material and to improve the NaOCl production along with zinc, copper, stainless steel, aluminum and titanium an electrode coated with Dimensionally Stable Anode (DSA) was tested. Titanium electrode coated with DSA was prepared by using a titanium sheet of 1.5 mm thickness, which was washed and cleaned thoroughly prior to being defatted with acetone. Finally, it was soaked in a 10% (w/w) acetic acid solution for 1–2 h at 90 °C. This treatment enhanced the micro porous structure of the material by removing the compact oxide layer on the surface. After washing with distilled water the sheet was placed in dehydrated alcohol to protect it from being oxidized again before the coating operation. A coating liquid was prepared according to the specification mentioned in Table 2 (all chemicals were ordered from Aldrich).

Table 2. Composition of coating reagent utilized in DSA preparation [5, 15, 16].

Reagents	Amount
RuCl ₃	1 g
36% HCl	0.5 ml
n-butanol	17 ml
Iso-propanol	10 ml
Ti(OC ₄ H ₉) ₄	3 ml
Ti:Ru	1:3.46

The prepared liquid was coated onto the cleaned and dried titanium sheet surface. Coating operation was carried out about 20 times and after each coating, the sheet was heated to a temperature of 410 °C and held for 20 min. To ensure complete dissolution of RuCl₃ and Ti(OC₄H₉)₄, and to harden the RuO₂-TiO₂ layer over the titanium sheet, the sheet was heated to 460 °C in the last heating operation and held for 2 h as specified in the literature [15]. A titanium cathode was used along with the DSA during electrochemical tests.

3. RESULTS AND DISCUSSION

The results of the NaOCl production study conducted using the seawater supplied to HUBCO Power Plant is detailed in this section.

3.1. Electrode material

During the investigation on electrode material zinc, copper, stainless steel, aluminum and titanium were tested as candidate materials. Effect of different electrode material on the production of NaOCl is presented in Figure 2. Temporal variation in Figure 2 shows that at times greater than 180 min the production of NaOCl was insignificant for both aluminum and copper. Both metals are considered as good conductors, easily available and are commonly being used in the electrolytic industry [17, 18]. However, low process efficiency for the production of NaOCl shows that aluminum and copper are unsuitable when utilized as electrode material (34 gm/l and 230 mg/l respectively). Although, application of the zinc electrode has been reported in the electrolytic industry, its potential to corrode rapidly render its usage less attractive. Both zinc and stainless steel electrodes are not selected due to insufficient production of NaOCl in this study (920 mg/l and 1010 mg/l respectively). Similar results are also reported in the literature [5].

Production of NaOCl reached about 1900 mg/l using the titanium electrodes. In addition, the electrode stability was observed to be better than other tested electrodes during experimental runs. Titanium is generally used in the electrochemical industry as cathode materials in electrochemical cells that produce chlorates and hypochlorite ions.

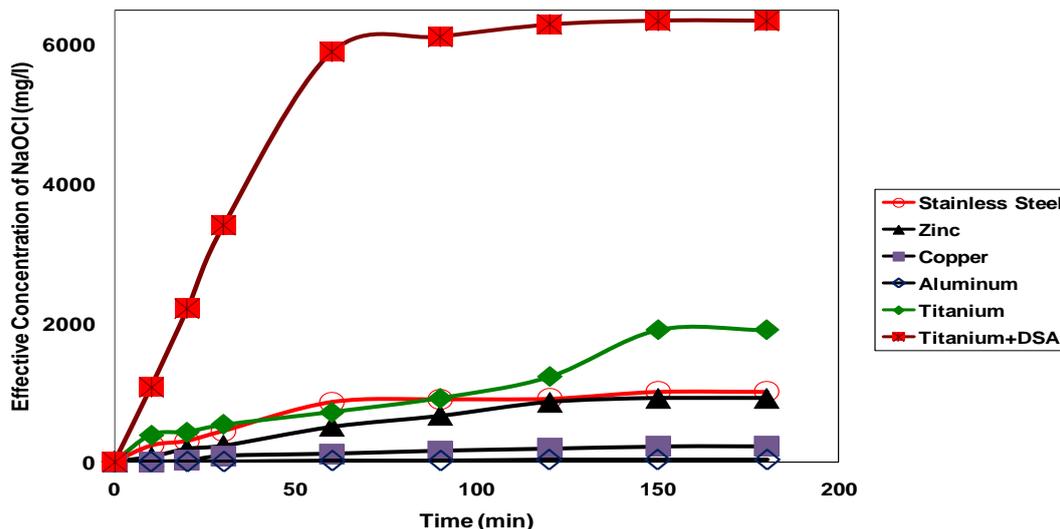


Figure 2. Temporal variation in the production of NaOCl using various electrode materials

In addition to that it has an average life of two years [5]. As the consumption of the electrode is directly related to the economics of the process consumption rate of electrodes were measured using the difference in initial and final mass of electrodes. Table 3 presents the comparison of mass of electrode materials consumed during 180 min run time. Results reveal that the consumption of the aluminum electrode is highest. This attribute is because of the higher dissolution ability of aluminum, as evidenced in the literature for fully consumable materials [17]. However, titanium is electrochemically the most stable material among those tested in this work.

Table 3. Comparison of electrode material consumption during 180 min test runs.

Electrode Material	Mass Consumed (g)
Aluminum	0.0148
Copper	0.0053
Zinc	0.0126
304-Stainless Steel	0.0119
Titanium	0.0015
Titanium with DSA coating	Below detection limit of 0.00001 g

Based on the results obtained and using the stability of the electrode materials during NaOCl production, titanium is superior in comparison to other counterparts. Titanium is the material of choice due to its good chemical resistance, higher breakdown potential and reasonable cost [19]. Finally, titanium electrode after DSA coating was tested for stability and NaOCl production. Titanium with DSA coated electrode showed excellent stability (as shown in Table 2) and production of NaOCl reached to about 6350 mg/l which was consistent with the literature [5]. In all subsequent experiments titanium electrode coated with DSA was used.

3.2. Relationship between current density and process efficiency

Appropriate current density has a great effect on the NaOCl production efficiency [20]. In this part of the study the effect of current density on the production of NaOCl using titanium-DSA electrodes was investigated. The current was varied between 16.4 to 112.3 mA/cm² in four experimental runs [21]. Temporal variation of NaOCl production at different current densities is shown in Figure 3. It was observed that the production of NaOCl had a direct relation with the run time as the production of NaOCl increased with rising current density. In contrast, efficiency of the process decreased when the current density increased beyond a value of 72.4 mA/cm². Using a current density of 72.4 mA/cm², the production of NaOCl reached a value of 7080 mg/l. As current density is directly related to the cost of production, it becomes necessary to use an optimum value of current density for efficient production and minimum cost. From the study, the current density of 72.4 mA/cm² was found to be most suitable for an efficient process of NaOCl production as evidenced in the literature [5, 21].

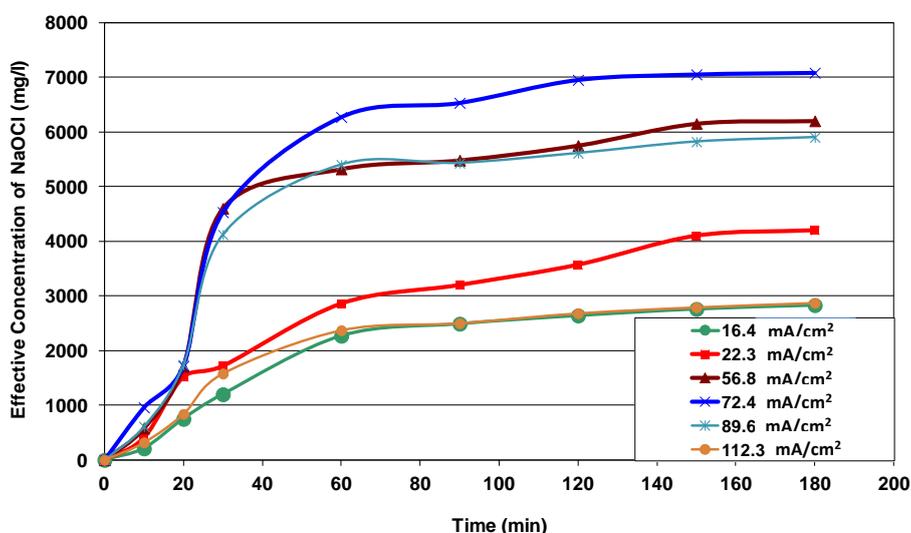


Figure 3. Temporal variation in the production of NaOCl at various current densities.

3.3. Relationship between anode to cathode surface area ratio and process efficiency

In this part of the study anode to cathode surface area ratio (S_a/S_c) was varied in six experimental runs. The relationship between the surface area ratio and produced NaOCl concentration is presented in Figure 4 showing the results of 30, 60, 120 and 180 min of runs. It can be seen from Figure 4 that by increasing the surface area ratio, production of NaOCl also increases almost linearly up to a surface area ratio of unity. Subsequently, the rate of the increase appears to decline slightly. However, a marginal increase in the NaOCl production is observed. This phenomenon may be attributed to the inhibition of some of the side reactions involved [13]. The results of this research corroborate earlier literature reports, claiming that a ratio of S_a/S_c of unity or thereabouts would augment the production of NaOCl and also reduce the cost of production [5, 21-23].

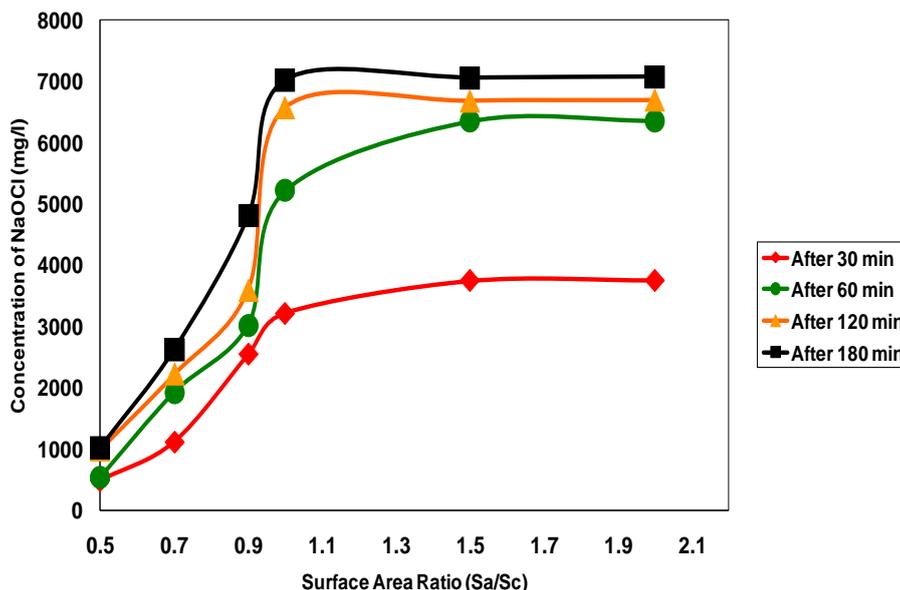
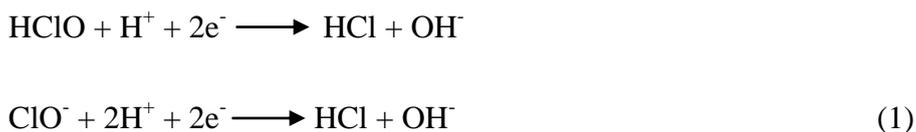


Figure 4. Effect of surface area ratio (S_a/S_c) on NaOCl production

The low generation of chlorine at lower ratios of the parameter S_a / S_c , can understandably be related to the fact that the electrochemical reduction of hypochlorite ion occurs at the cathode according to the following reactions [13]:



As can be seen from Figure 4, the increase in the production of NaOCl below a surface area ratio of unity appears to be linear. However, beyond the surface area ratio of unity, the concentration appears to increase but at a much less significant rate than at surface area ratios below unity. As a result, it appears practical to select a surface area ratio of 1 as this value is likely to reduce operating costs as reported for results obtained in a similar work [5, 11].

3.4. Relationship between inter-electrode spacing and process efficiency

Inter-electrode spacing plays an important role in an electrochemical process with respect to process efficiency and production cost. The variation in NaOCl production with time at a different inter-electrode spacing (2.5 to 11.5 cm) is presented in Figure 5. It can be seen from Figure 5 that the rate of NaOCl production is inversely related to the inter-electrode spacing. Maximum production of NaOCl was achieved at a spacing of 7 cm. Furthermore, minimizing the inter electrode spacing resulted in no appreciable increase in process efficiency. One may observe from Figure 5 that the production of NaOCl at a spacing of 4 cm is approximately equal to the spacing of 10 cm. Therefore 7 cm inter electrode spacing appeared to be a reasonable choice for effective NaOCl production. This

value of 7 cm is comparable to a recently reported optimum inter-electrode spacing of 8 cm using a very similar experimental set-up [5].

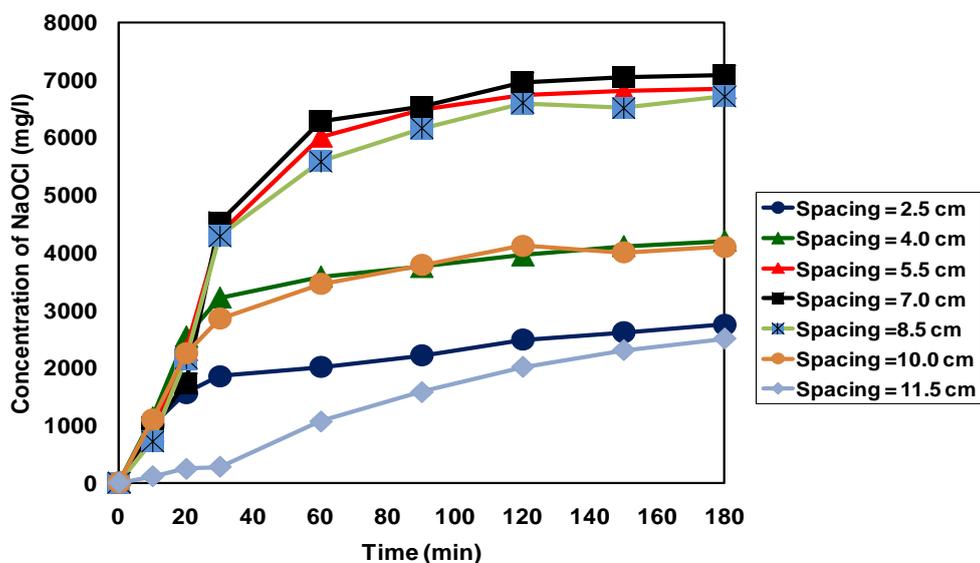


Figure 5. Effect of inter-electrode spacing on NaOCl production

4. CONCLUSION

Problems associated with the use of seawater for cooling and other purposes in the power industry necessitate the control of microbiological growth in the pumping and piping system. At HUBCO Power Plant, the traditional disinfection system was required to be replaced with a new and effective system. Therefore, an onsite electrochemical process was undertaken in the present study to establish the operating conditions for the production of sodium hypochlorite (NaOCl) disinfectant. The research arrived at the following conclusions:

1. Titanium electrode coated with DSA demonstrated excellent stability as compared to other tested electrode materials and production of NaOCl reached to an optimum value of about 6315 mg/l, which was consistent with the literature.
2. A current density of 72.4 mA/cm^2 was found to be a promising value for an efficient production of NaOCl and was consistent with the values reported in the literature.
3. An anode to cathode surface area ratio of unity was found to be the most advantageous value for an efficient production of NaOCl and reduced operating cost.
4. Inter-electrode spacing was found to be an important parameter with respect to the process economy. An inter-electrode spacing of 7 cm was found to be a better value giving the highest production of NaOCl.

In the future it is recommended to design suitable experiments to optimize the figures of merit in a more scientific manner. As it is, the recommendations in this study can be implemented well

within HUBCO's existing infrastructure, thus improving the efficiency of the power plant in the long term.

ACKNOWLEDGEMENTS

NED University of Engineering and Technology, the University of Malaya Research Grant RG096/10AET and the University of Malaya's Bright Sparks Funding {Bsp_App462/11(K)} are gratefully acknowledged for providing financial support.

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