ON-SITE GENERATION OF SODIUM HYPOCHLORATE

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ABSTRACT

This research involves generation sodium hypochlorite instantaneous and on-site to meet domestic requirement such as water treatments in electrical power station; by using electrochemical cell constructing of titanium cathode and titanium coated with ruthenium dioxide-platinum metal anode.

Many operational conditions in Dimensionally Stable Anode cell were studied such as temperature 8-45o C, space electrodes 2-6 mm, current density 2.5-20 A/dm2, flow rates 25-65 ml/min. The study indicated using 3 % sodium chloride solution, pH=8, operating temperature 13-39o C, space electrodes 4 mm, current density 20 A/dm2, flow rate 45 ml/min produced 0.2 % hypo by DSA cell. In order to increase concentration of hypo to 0.8 % ± 0.1, four cells in series were used.

INTRODUCTION

On–site sodium hypochlorite generation required to obtain disinfecting water has beneficial advantages because it is cost-effective, easy to produce and eliminates potentially dangerous handling and storage problems associated with other types of disinfection practices. On–site sodium hypochlorite (NaOCl) generation requires only salt, water and electricity to produce sodium hypochlorite and allows the user to produce the amount of sodium hypochlorite actually needed unlike conventional 12 to 14% purchased hypochlorite, which will degrade over time, sodium hypochlorite generated on-site will–maintain its strength. In addition, where purchased hypochlorite breaks down it degrades to oxygen and chlorates [1].

The process of generating sodium hypochlorite involves dissolving solar grade salt with water to form a concentrated brine solution. The concentrated brine solution is then diluted and passed through an electrolytic cell. In the process of on-site sodium hypochlorite generation 1 kg of equivalent chlorine can be generated from 3.5 kg of salt [2].

Different types of anodes were used by different authors such as titanium coated with ruthenium dioxide, palladium oxide, titanium dioxide, iridium dioxide, rhenium dioxide, platinum metal were used to obtain sodium hypochlorite in low concentration below 1% on-site for instantaneous production [3]. Mixture of platinum, iridium dioxide, and ruthenium dioxide were used to improve the stability of the anode with long life up to 5 years in service. This anode can be used in cold weather down to 5o C. This anode was formed by heating a layer of an organic solution containing the halides of metals applied on to substrate by brushing or by immersion or by any other known method of application [4,5].

Mixture of ruthenium dioxide, iridium dioxide, titanium dioxide will be control the production of sodium hypochlorite with limited amounts of side reactions and with lower voltage drop at the electrolytic solution [6,7].

Reactions of either oxygen or chlorine with the electrodes control and limit the electrode choice, since the exchange current densities of these platinum group on the oxygen electrode reaction are as follows [8]:

Ru>Ir>Rh>Pd>Pt

But the exchange current densities on the chlorine electrode reactions are as follows:

Pd>Ru>Ir>Rh>Pt

Since smaller generation of oxygen and superior activity on the chlorine electrode reaction, palladium is acceptable. But palladium is soluble, therefore anti-corrosive

electrodes made of a Pt-Pd alloy or coating Pt-Pd on the substrate were recommended [8,9].

The palladium oxide anode is soluble during electrolysis and it can not be practically used because of inferior anti-corrosive. Therefore anode coated with mixture of ruthenium dioxide-platinum metal was studied.

There are different possibilities by different workers explaining the mechanism of chemical reaction to produce the sodium hypochlorate. The controlling factor in electrolysis is the type and composition of anode which called electrocatalyst. The mechanism for electrochemical reactions of solution in order to produce hypochlorate by the reaction of chlorine with water was reported by Shilov et al [10] and Lifshitz [11].

EXPERIMENTAL WORK

Dimensionally stable anodes are usually made of ruthenium or iridium dioxide deposited on titanium. Their use favours chloride oxidation and hypochlorite reduction to limited value. Titanium was treated by trichloroethylene liquid, then the surface was washed by 5% hydrofluoric acid solution followed by washing with water

A commercial titanium alloy (Ti-38A) sheet measuring 5 X 5, was coated by brush with solution containing 2 g., of (Hexachloroplatinic acid) and 1 g., of ruthenium trichloride dissolved in 20 ml isopropyl alcohol, 2.5 ml hydrochloric acid was added to the above solution then followed by adding 5 ml., of cedar wood oil [3].

The coated titanium electrode was dried in 150o C in electrical oven for 10 min. The coated titanium electrode was heated in air at 500o C for one hour this procedure was repeated seven times in order to insure higher coating layers. The seventh coated layer was heated for 1½ hr to obtain complete oxidation .The coated layer was evaluated by X-ray deffractometer which indicates that the coating is made up of 50% (by wt) ruthenium oxide and 50 % (by wt) metallic platinum.

The prepared anode 5 X 5 cm., was made up from DSA. The cathode 5 X 5 cm., was made up from commercial titanium alloy. Both anode and cathode were immersed completely in the 3% sodium chloride solution. Different current densities were used that is i.e 20 A/dm2, 10 A/dm2, 5A/dm2, & 2.5 A/dm2 as shown in Tables (1, 2, 3, & 4). The following studies were conducted at constant Temp. = 25o C, pH = 8 and 3% sodium chloride solution. Different electrode separations were studied such as 2 mm, 4 mm and 6 mm under different current densities from 5 A/dm2, 10 A/dm2, 15 A/dm2, 20 A/dm2 & 25 A/dm2 in order to obtain required voltage of the cell, as shown in Table (5).

Similarly different flow rates from 25 ml/min up to 65 ml/min were studied at constant 4 mm electrode separation and constant current density (20 A/dm2), as shown in Table (6) .

Different temperature from 8o C up to 45o C were investigated at constant current density (20 A/dm2) and 4 mm electrode separation and constant flow rate (45 ml / min) as shown in Table(7).

Series and parallel cells connection were studied in order to obtain suitable cell connection for higher sodium hypochlorite production as shown in Tables (8 & 9).

Sodium hypochlorite analysis was conducted by sodium thiosulphate, potassium iodide, and glacial acetic acid using starch indicator. Sodium chloride was evaluated by silver nitrate using potassium dichhromate as indicator [2].

RESULTS AND DISCUSSION

Dimensionally stable anode gave higher concentration even though they were expensive. The electrode gave less side reaction by directing the chemical reaction site. ruthenium dioxide acts as catalyst and platinum gives limited oxygen production. Tables (1, 2, 3, & 4) and Figs., (1,& 2) indicated that conversion increases with time but current efficiency of hypochlorite production decreases with time for 2.5 A/dm2, 5 A/dm2, 10 A/dm2 and 20 A/dm2 at constant pH = 8, temperature = 25o C and sodium chloride concentration 3% .

The results also showed that hypochlorite increase with time. The results indicated that current efficiency decrease with longer time

because the rate of hypochlorite formation start to approach the rate of hypochlorite consumption tell equilibrium reach , where rate hypochlorite formation equals rate of hypochlorite consumption . Therefore a shorter time of electrolysis is preferred.

The current efficiency increases to high value at very short time. This will lead to small conversion as shown in Fig. (2). Hence at 5-10 % conversion gave a high current efficiency which can be used in continues dynamic conditions.

Therefore it is best to obtain 0.2 % sodium hypochlorite instead of 0.8 % hypo in continues process.

Table 1 Hypochlorate concentration at different times at constant current density 2.5 A/dm^2

No	Time hours	Product NaOCl (g/L)	Un reacted NaCl (g/L)	Conversion %	Current efficiency %
1	0.5	0.4	25.5	5.0	92.0
2	1.0	0.7	27.7	7.6	80.0
3	1.5	1.0	27.3	9.0	77.0
4	2.0	1.1	27.0	10.0	63.0
5	2.5	1.3	26.7	11.0	60.0
6	3.0	1.5	26.4	12.0	59.0
7	3.5	1.7	26.3	12.5	56.0
8	4.0	1.8	26.1	13.0	52.0

- RuO_2-Pt / Ti (DSA)Anode
- Titanium Cathode
- PH = 8
- Current density 2.5 A/dm^2
- Temperature = 25° C
- 3 % NaCl

Table 2 Hypochlorate concentration at different times at constant current density 5 A/dm^2

No	Time hours	Product NaOCl (g/L)	Un reacted NaCl (g/L)	Conversion %	Current efficiency %
1	0.5	0.4	25.5	5.0	92.0
2	1.0	0.7	27.7	7.6	80.0
3	1.5	1.0	27.3	9.0	77.0
4	2.0	1.1	27.0	10.0	63.0
5	2.5	1.3	26.7	11.0	60.0
6	3.0	1.5	26.4	12.0	59.0
7	3.5	1.7	26.3	12.5	56.0
8	4.0	1.8	26.1	13.0	52.0

- RuO_2-Pt / Ti (DSA)Anode
- Titanium Cathode
- PH = 8
- Current density 2.5 A/dm^2
- Temperature = 25° C
- 3 % NaCl

The effect of using different electrode separation on the internal resistance of the cell can be seen from the voltage / current relation ship as illustrated in Table (5) Fig.,(3). The best electrode separation was found to be 4 mm in order to generate hypo. Since lower electrode separation will result in hypo decomposition and high electrode separate will slow hypo generation. The resistance of the cell is decreased, if the gap between the electrodes is decreased. The closer the gap between the electrodes, the greater the efficiency of the current.

Table 3 Hypochlorate concentration at different times at constant current density 10 A/dm^2

No	Time hours	Product NaOCl (g/L)	Un reacted NaCl (g/L)	Conversion %	Current efficiency %
1	0.5	1.55	27.9	7.0	89.0
2	1.0	2.60	26.7	11.0	75.0
3	1.5	3.51	25.9	13.5	67.5
4	2.0	4.20	25.5	15.0	60.0
5	2.5	4.95	25.2	16.0	57.0
6	3.0	5.73	25.1	16.5	55.0

- RuO_2-Pt / Ti (DSA)Anode
- Titanium Cathode
- PH = 8
- Current density 10 A/dm^2
- Temperature = 25° C
- 3 % NaCl

Table 4 Hypochlorate concentration at different times at constant current density 20 A/dm^2

No	Time hours	Product NaOCl (g/L)	Un reacted NaCl (g/L)	Conversion %	Current efficiency %
1	0.5	3.0	27.2	9.3	86.0
2	1.0	5.0	25.5	15.0	72.5
3	1.5	6.9	24.6	18.0	66.0
4	2.0	7.6	24.0	20.0	55.0
5	2.5	8.7	23.4	22.0	50.0

- RuO_2-Pt / Ti (DSA)Anode
- Titanium Cathode
- PH = 8
- Current density 20 A/dm^2
- Temperature = 25° C
- 3 % NaCl

Table 5 Current density vs. electrode separation for (RuO_2-Pt/Ti anode and titanium cathode) single cell

No	Current densities (A/dm^2)	Volts (V)		
		2 (mm) Electrode separation	4 (mm) Electrode separation	6 (mm) Electrode separation
1	5	3.20	3.40	3.55
2	10	3.60	3.90	4.20
3	15	4.20	4.45	4.80
4	20	4.65	4.90	5.45
5	25	5.20	5.50	6.10

- 3 % NaCl
- PH = 8
- Temp. = 25° C

The behavior of different flow rate of 3 % sodium chloride solution using dozing pump on the current efficiency for hypochlorite production were studied in order to obtain maximum current efficiency. The results indicated that maximum current efficiency were observed when flow rate was 45 ml/min which gave about 81 % current efficiency as shown in Table (6) and Fig. (4).

Table 6 Effect of flow rate on current efficiency for (RuO_2-Pt/Ti anode and titanium cathode) single cell

No	Flow Rate (ml/min)	Product NaOCl (g/L)	Current efficiency %
1	25	2.80	60.0
2	30	2.72	70.0
3	35	2.53	76.5
4	40	2.30	80.0
5	45	2.10	81.0
6	50	1.85	80.0
7	55	1.60	76.0
8	60	1.35	70.0
9	65	1.10	61.5
• 3 % NaCl • PH = 8 • Current Density 20 (A/dm^2)		• Temp. = 25° C • Electrode Separation 4(mm)	

Higher temperature over 39°C will not affect current efficiency (i.e 81 %) . After that (above 40°C), current efficiency will be decreased due to conversion of hypo to sodium chlorate as shown in Table (7) and Fig. (5). Hence the recommended operational temperature could lie between 13° C up to 39° C to avoid undesirable behavior. This range of temperature (13°C–39°C) is suitable to the ambient water flowing temperature in Iraq [12].

Table 7 Effect of temperature on current efficiency for (RuO_2-Pt/Ti anode and titanium cathode) single cell

No	Temperature °C	Product NaOCl (g/L) ± 0.1	Current Efficiency %
1	10	1.95	76
2	15	2.00	80
3	20	2.00	80
4	25	2.00	80
5	30	2.00	80
6	35	2.00	80
7	40	1.98	77
8	45	1.60	62
• 3 % NaCl • PH = 8 • Current density 20 A/dm^2		• Electrode Separation 4 mm • Flow rate 45 mL/min	

The above results were conducted on a single stage cell using parallel two cells to increase the product to double values by increasing the flow to twice but obtaining the same concentration of produced hypochlorite. But using two cells in series and keeping the flow rate constant the concentration of produced hypo from 0.2% up to 0.4% as shown in Table (8).

The active sodium hypochlorite production obtained with this configuration is presented in Fig (6). The production increases linearly with the current density. Table (9) summarizes the performance achieved by the different pattern cells. The current efficiency stabilizes around 78 % for various current densities.

Table 8 Different pattern of flowing cells

Flowing Pattern	One Cell	Two Cells in parallel	Two Cells in series	Three Cells in series	Four Cells in series
Flow rate (ml/min)	45	90	45	45	45
Current density (A/dm^2)	20	20	20	20	20
NaOCl product (g/L) ±0.1	2	2	4	6	8

Table 9 Sodium hypochlorate production at different current density in single cell flow 45 ml/min

Current density (A/dm^2)	5	10	15	20
Product NaOCl (g/hr)	1.3-1.4	2.6-2.7	3.9-4	5.4-5.5
Current efficiency %	78	77	75	80

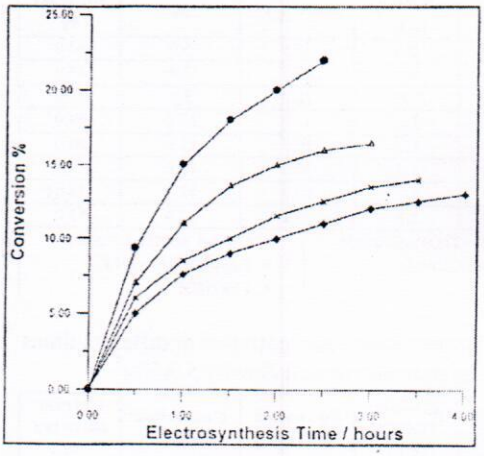

Fig.(1) Influence of the current density on the conversion for DSA

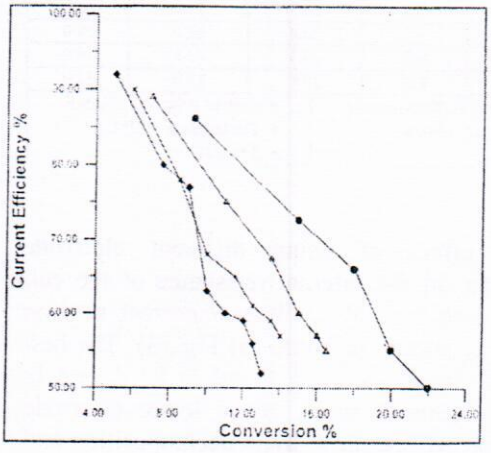

Fig.(2) Evolution of the current efficiency with the conversion rate for DSA anode with different current densities.

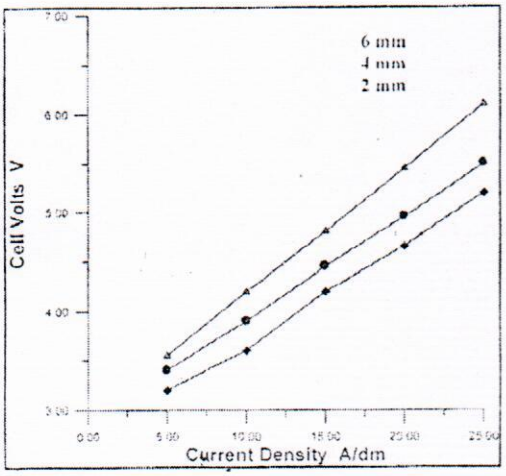

Fig. (3) Effect of electrode separation on cell characteristics for DSA anode

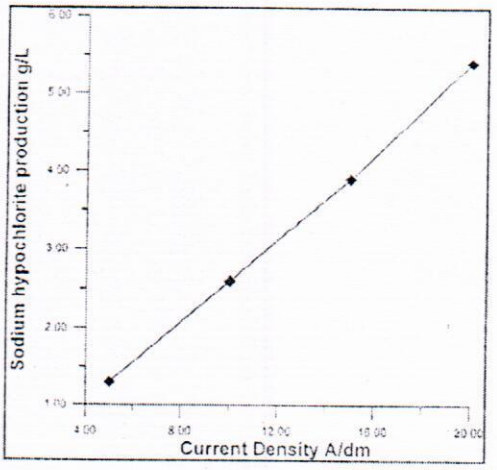

Fig.(6) Influence of the current density on the hypo product in cells flow

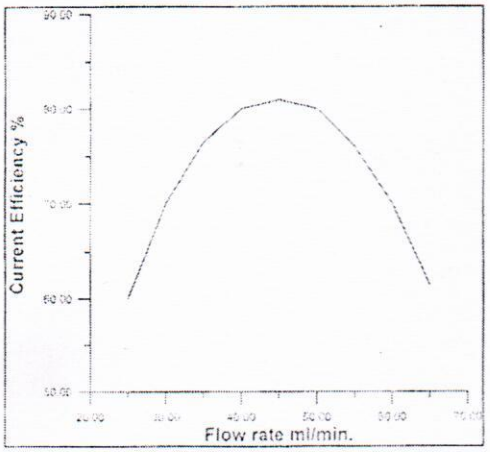

Fig. (4) Effect of flow rate on current efficiency for DSA anode

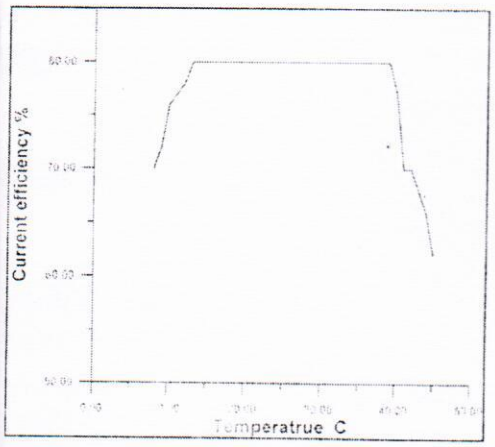

Fig. (5) Effect of temperature on current efficiency for DSA anode

CONCLUSIONS

1. Ruthenium dioxide–Platinum /titanium anode (DSA) and titanium cathode are more efficient and not affected by chemicals uses.
2. At the best operational conditions of the work are temp. = 13-39° C, space electrodes 4 mm., current density 20 A/dm^2, 45 ml/min., flow rate to produce 0.2 % hypo.
3. Higher hypo-concentration up to 0.8% needs four cell in series.
4. Hypo production rate is directly proportional to current density.

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