



Optimizing Process Condition in Sodium Chlorate Electrolyzer to Improve Lifespan Produce

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Abstract. Sodium chlorate (NaClO_3) is produced from two undivided electrolysis cells, where the oxidation reaction of sodium chloride (NaCl) to chlorine occurs on the anode side, and the reduction of water (H_2O) to hydrogen occurs on the cathode side. In the process production, requires considerable electrical energy which reaches 5.05 MWh per ton of sodium chlorate. With an average energy efficiency of 95% on an industrial scale, improvements are still needed to increase energy efficiency and prevent excessive energy consumption. This study aims to optimize process conditions of electrolyzer (e.g. flowrate, voltage, and current), hence maintaining the electrolyzer performance and running well as long as possible. The results showed that the voltage and resistance of the electrolyzer increase over the time and electrical energy consumption per ton of sodium chlorate will increase too. Interestingly, increasing production capacity (up to 58.24%) will increase the flowrate and electric current in the electrolyzer and will reduce the resistance value (up to 31.25%). Performing an acid wash process in a certain period on the electrolyzer is useful to keep the voltage value from continuing to increase. These two processes will reduce the total electrical energy consumption and prevent excessive energy consumption by continues process production.

Keywords: Wear Resistant, Bucket Teeth, Tempering, Low Alloy Steel, Heat Treatment.

1 INTRODUCTION

In industry, sodium chlorate (NaClO_3) is widely used as a raw material for the manufacture of environmentally friendly chlorine dioxide (ClO_2) in the pulp bleaching process [1]. Sodium chlorate (NaClO_3) is produced in situ process in integrated chlorine dioxide technology or importing from somewhere if chlorine dioxide (ClO_2) manufacturing technology uses single-vessel processes (SVP) technology or called non-integrated chlorine dioxide technology. The selection of technology in the manufacture of chlorine dioxide (ClO_2) will consider the overall process, raw materials used, by-products or waste produced, and the purity of chlorine dioxide (ClO_2) produced [2]. However, the most decisive aspect is the overall total production cost to produce every single ton of chlorine dioxide (ClO_2). The most widely used in the pulp and paper industry is integrated chlorine dioxide technology, as it offers a low-cost method of producing chlorine dioxide (ClO_2) without the requirement to import crystal

sodium chlorate (NaClO_3) as the main chemical. By making sodium chlorate (NaClO_3) in-situ, the process offers a reliable supply and avoids dependence on the market, while eliminating the cost, uncertainty, safety and administrative issues of importing and storing large quantities of sodium chlorate (NaClO_3), sulfuric acid (H_2SO_4), methanol (CH_3OH) and peroxide ion (H_2O_2).

Sodium chlorate (NaClO_3) is produced in-situ within integrated chlorine dioxide technology through electrolysis process. The electrolysis process to form sodium chlorate (NaClO_3) consumes significant amounts of electrical energy, around 70% of the total production cost. Almost half of the electrical energy used ends up as unrecoverable losses as a result of the ohmic drop (IR drop) of the electrolyte solution between the electrodes and the overvoltage required for the reaction to occur at each electrode. A typical electrolyte solution in the sodium chlorate (NaClO_3) production process consists of 450 - 650 gpl sodium chlorate (NaClO_3), 100 - 120 gpl sodium chloride (NaCl), 1 - 4 gpl sodium hypochlorite (NaOCl), 1 - 6 gpl sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), bulk electrolyte pH 6.0 - 6.5 and bulk electrolyte solution temperature 70 - 85°C. The electrolyte solution may also contain sodium perchlorate (NaClO_4) which should not be greater than 100 gpl. A high concentration of sodium chlorate (NaClO_3) is essential in the separation process by the crystallization method and a high concentration of sodium chloride (NaCl) is essential in the anode operation [3].

At the beginning of the sodium chlorate (NaClO_3) process was discovered, the process runs very inefficiently with a current efficiency of only about 37% [4], but the modern sodium chlorate (NaClO_3) manufacturing process has development and the optimal value of current efficiency on an industrial scale can be obtained by 92% - 95%. Where an increase in current efficiency value though only a few percent will have a considerable economic and environmental impact, because it is related to the consumption of electrical energy which is quite large and the resulting production capacity. It takes about 5.05 MWh of electrical energy to produce one ton of sodium chlorate (NaClO_3) [3]. Some of the reasons that cause losses in current efficiency and making production cost is over is due to side reactions that occur at the electrode, therefore the characteristics of the electrode in the process of making sodium chlorate (NaClO_3) become very important. In addition, the loss of current efficiency (ϵ) also occurs in the reaction that takes place in the electrolyte solution, so it requires special attention to the process control that takes place [5].

Side reactions that cause a loss of current efficiency and increasing electrical energy consumption will be seen in the total voltage and resistance that occur in the cell electrolyzer system during the sodium chlorate (NaClO_3) manufacturing process. The study aims to optimize process conditions so that the electrolysis process continues to run well and the electrical energy consumption per ton of sodium chlorate (NaClO_3) produced does not continue to increase significantly. As comparison, process conditions without any modification and electrolyzer performance are recorded and discussed.

2 METHODOLOGY

2.1 Data Source

All data is obtained from the actual chlorine dioxide plant X with integrated technology from Canada and has been more than 10 years old. The process parameters of the electrolyzer cell are pressure 20 Kpa, temperature 85oC and pH of electrolyte solution 5.8 - 6.2 are controlled by DCS operator by put set point in DCS screen and processes by DCS data based and action by control valve in field to catch up input set point. All process parameters of the cell electrolyzer comes from existing instrumentation in the field. The data will be processed in the distributed control system (DCS) database and recorded in a process plant information software as shown at Figure 1. Historical data will be seen as information about plant and saved in process plant information software. The data will be utilized as back up data for troubleshooting, equipment performance evaluation and also some data will be extracted into Microsoft Excel to be used as a daily report production. The data that has been extracted into Microsoft Excel will be used as a calculation data at next step.

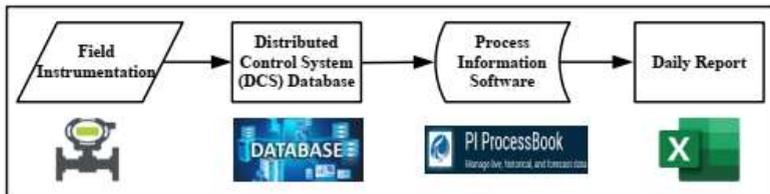


Fig. 1. Data Collection and Processing.

2.2 Data Calculation

The cell electrolyzer system used a schematic multi monopolar arrangement as shown in Figure 2. Consists are 78 electrolyzers. Each electrolyzer consists of 56 anodes and cathodes with a distance of ± 3 mm. The data of voltage, flow rate and electric current are the data of the whole arrangement of the cell electrolyzer system. This study will look at the phenomenon if there is only 1 anode and 1 cathode. Data electric current, flow rate, electrical energy consumption and product are the result of the dividing of 78 electrolyzers and 56 electrode pairs. While the resistance is the result of the calculation of the current and voltage.

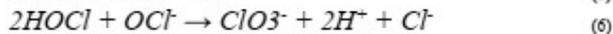
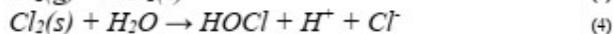
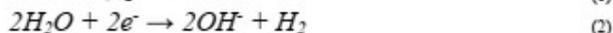


Fig. 2. Multi Monopolar Electrode Arrangement.

3 RESULT AND DISCUSSION

3.1 Sodium Chlorate (NaClO₃) Production

Sodium chlorate (NaClO₃) is produced from a series of electrolysis processes of sodium chloride (NaCl) solution, first reaction where chlorine gas (Cl₂) is formed from the oxidation of sodium chloride (NaCl) on the anode side in Equation (1) and hydrogen gas (H₂) is formed from the reduction of water (H₂O) on the cathode side in Equation (2). The second reaction is a homogeneous reaction that occurs between chemical compounds that have been formed in the electrolyte solution [5]. The whole reaction occurs in one part of the cell electrolyzer which is usually called the chlorate cell.



Chlorine gas (Cl₂) formed on the anode side is in the gas phase, but it is quickly dissolved in its electrolyte solution as in Equation (3). Furthermore, the dissolved chlorine (Cl₂) will hydrolyze to form hypochlorous acid (HOCl) compounds as in Equation (4). This reaction occurs very close to the anode side and causes a low pH in the electrolyte solution as a whole system. In the electrolyte solution, some of the hypochlorous acid (HOCl) will deprotonate due to equilibrium and produce hypochlorite (OCl) compounds as in Equation (5). Furthermore, the hypochlorous acid (HOCl) compound will react with the hypochlorite (OCl) compound in the electrolyte solution to produce chlorate (ClO₃) as in Equation (6).

Table 1. Sodium Chlorate Production in Maintained Flowrate Condition.

Day	Current (A/h)	Flowrate (liter/h)	Voltage (volt)	Resistance (ohm)	Product NaClO ₃ (kg/h)	Power (kWh)	MWh per ton NaClO ₃
Day 1	13.34	5.40	2.83	0.21	0.56	84.70	6.33
Day 2	13.34	5.40	2.85	0.21	0.55	84.04	6.31
Day 3	13.03	5.40	2.87	0.22	0.56	82.91	6.21
Day 4	12.49	5.40	2.89	0.23	0.55	79.85	6.02
Day 5	12.29	5.40	2.89	0.24	0.55	78.59	5.90

Day 1 until day 5 in Table 1, flowrate of electrolyte solution going to cell electrolyzer is maintaining stable and the electric current slightly decreases, even though the sodium chlorate (NaClO₃) produced is relatively the same. There is an external factor that is not discussed in this study because it is related to the evaporation process of the water content electrolyte solution in the up-stream electrolysis process of the chlorine dioxide plant, that is will be affect to concentration of sodium chlorate (NaClO₃) at the inlet electrolyte cell electrolyzer. With concentration target of sodium chlorate (NaClO₃) at the outlet of cell electrolyzer is 478.91 gpl, the higher

concentration of sodium chlorate (NaClO_3) at the inlet electrolyte solution going to cell electrolyzer, the less electric current is required in the process of electrolysis sodium chloride (NaCl) on both electrodes. Based on laboratory analysis at chlorine dioxide plant X, on day 1 until day 5, the inlet sodium chlorate (NaClO_3) concentration at the inlet electrolyte solution going to cell electrolyzer increased from 322.79 gpl to 349.77 gpl. However, this condition did not cause the voltage and resistance in the cell electrolyzer decrease because the amount of electric current used also decreased. Voltage and resistance of the cell electrolyzer actually increase during the electrolysis process.

The increasing voltage and resistance in the cell electrolyzer along with electrolysis process, will increase the overall electrical energy consumption per ton sodium chlorate (NaClO_3) produced. Although the amount of electrical energy consumption seems lower, the electrical energy consumption per ton of sodium chlorate (NaClO_3) will actually increase. It can be seen in Table 1 that the average electrical energy consumption to produce average 0.55 kg/hr of sodium chlorate (NaClO_3) in 5 days by maintaining flow rate stable is 6.15 MWh, meanwhile the average consumption of electrical energy to produce one ton of sodium chlorate (NaClO_3) is around 5.05 MWh [3]. Even only 1.1 MWh excessive electrical energy consumption, this amount would be large if applied on industrial scale with processes running for 360 days a year. With condition as shown in Table 1, reaction in Equation 1 until Equation 6 will happens at single anode and cathode in cell electrolyzer arrangement. Over the times electrolysis process, when the voltage value increases, the resistance value of the cell electrolyzer system will increase linearly as shown in Figure 3. If looking from reaction happens in cell electrolyzer system, this condition happens due to several thing, that is because corrosion reaction at cathode side, deposit on the anode side because impurities from side reaction, hydrogen gas (H_2) bubble in the electrolyte solution and thickness reduction of both electrodes side due to shutdown process. But if looking from properties of both eletrodes, that is because natural resistance from mechanical properties of anode and cathode used, distance between the anode and cathode and resistance of the electrolyte solution itself.

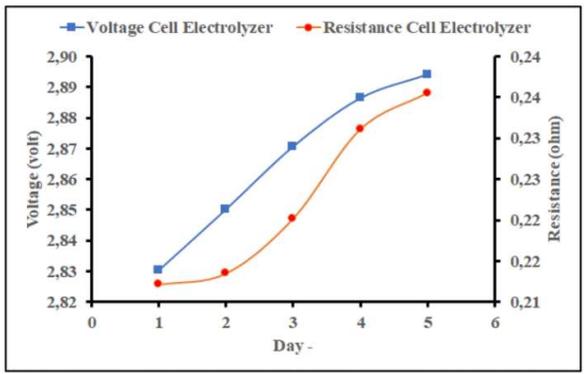


Fig. 3. Relation Between Voltage and Resistance at Cell Electrolyzer When Current and Flow Stable.

The anode that is widely used in the sodium chlorate (NaClO_3) manufacturing industry is using titanium material coated with ruthenium compounds or commonly referred to as Dimensionally Stable Anode (DSA). DSA is widely used on an industrial scale because it is a good metal mixture as a barrier to the catalytic reaction of hypochlorite (OCl) decomposition in the sodium chlorate (NaClO_3) formation reaction and has a large electrocatalytic area [6]. For each coating on DSA measuring $10\ \mu\text{m}$ with 300 layers of granules, this causes thousands of times the increase in area. While the cathode used mild steel material which has the advantage of being resistant to impurities contained in the electrolyte solution, easy to produce, has a competitive economic value, has a low corrosion rate when in electrolyte solution during shutdown and has high stability (resistant to mechanical processes that occur as a result of gas bubbles and not detrimental to hydride formation) when the hydrogen evolution reaction (HER) process takes place [7]. The new anode and cathode have smooth and uniform surfaces. However, due to the corrosion reaction that occurs during the electrolysis process, the surfaces of the anode and cathode become not smooth and uniform anymore and increasing total voltage. Figure 4 shows the difference between cathode anode in new condition and the cathode anode after being used in the electrolysis process several times.

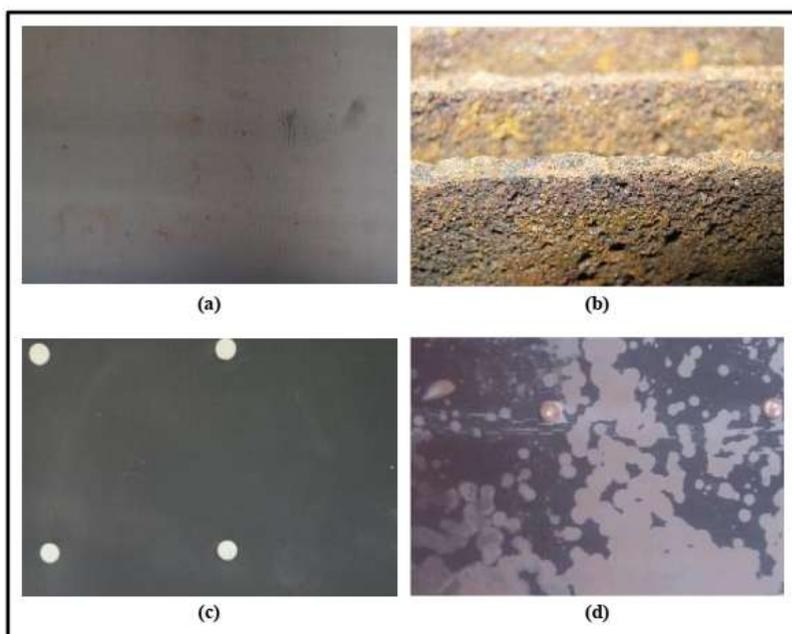


Fig. 4. (a) New Cathode Condition. (b) Old Cathode Condition. (c) New Anode Condition. (d) Old Cathode Condition.

Even sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) has been added to electrolyte solution, which one of function as cathode corrosion inhibitor rate and substantially extends the lifetime [8]. However, presence of sodium sulphate (Na_2SO_4) within electrolyte solution will increase the corrosion rate of the metal used as the electrode in the electrolysis process [5]. Sodium sulphate (Na_2SO_4) comes from makeup brine solution (liquid sodium chloride) into electrolyzer when concentration of sodium chloride (NaCl) is too low within electrolyte solution. Generally, the concentration of sodium sulphate (Na_2SO_4) contained in the brine solution (liquid sodium chloride) is around 2.5 - 5.5 gpl. Another problem is the extreme corrosion process that occurs in the electrolyte solution due to the attack of active chlorine on the mild steel cathode when the electric current is off during the shutdown or cathodic protection is failure. This not only shortens the life of the cathode used, but also causes small pieces of mild steel to be present in the electrolyte solution. This can cause short circuits and disruption of circulation in the cell electrolyzer system [3].

3.2 Process Modification to Improve Power Consumption

If the conditions in Table 1 are maintained for a long period, total electrical energy consumption per ton sodium chlorate (NaClO_3) will continue increase over the time related to the increasing voltage and resistance values of the cell electrolyzer system. Aim to make sure process running well and the electrical energy consumption is not too much over, and production of sodium chlorate (NaClO_3) still achieved, several process modifications are made to reduce the resistance value of the cell electrolyzer system, one of which is to increase the sodium chlorate (NaClO_3) production capacity. The more sodium chlorate (NaClO_3) produced, it will be directly proportional to the flow rate of sodium chlorate (NaClO_3) through the cell electrolyzer system and electric current that's passing through both electrodes. Increasing of sodium chlorate (NaClO_3) flow rate in the cell electrolyzer system, causing deposit - deposit at the surface of cathode and anode to be released and carried over to the next process and reduce the resistance value of the cell electrolyzer system as shown in Figure 5. However, the increasing of electric current will also increase the total electrical energy consumption, this is related to the production rate and will be proportional to the total sodium chlorate (NaClO_3) produced. But overall, the electrical energy consumption per ton of sodium chlorate (NaClO_3) will be lower than just keeping production rate stable or decreased.

Although resistance of cell electrolyzer system decreases with the increasing sodium chlorate (NaClO_3) production, voltage value of the cell electrolyzer system will still continue increase during the process. This is because during the electrolysis process, several things triggering increasing voltage value as mentioned in the previous sub-bab will continue to occur. To keep the voltage value from continuing to rise up and causing more electrical energy consumption, an acid wash procedure is carried out on the anode and cathode of the cell electrolyzer system. The acid wash process on the cell electrolyzer system is carried out by soaking the entire cell electrolyzer system using hydrochloric acid (HCl) solution with a concentration of 5 - 8% for approximately 1 hour. However, there are negative things that happen to cell electrolyzer during the acid wash process, anode and cathode will be submerged in an electrolyte solution containing hypochlorite (OCl) compounds without any electric current flowing. Corrosion rate at cathode will drastically increase and erosion of the coating on surface

anode side will happen. Hypochlorite (OCl) is a compound formed from a series of reactions that occur in the cell electrolyzer system. Hypochlorite (OCl) that is formed will react with hypochlorous acid (HOCl) to further produce sodium chlorate (NaClO₃).

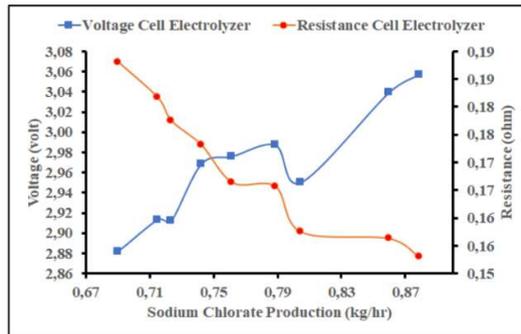


Fig. 5. Relation Between Voltage and Resistance at Cell Electrolyzer When Increasing Production Rate.

The process of increasing the corrosion rate at the cathode and eroding the coating on the anode surface occurs during the emptying out process of the cell electrolyzer before the inclusion of 5 - 8% HCl solution, and during the filling back process the electrolyte solution into the cell electrolyzer system. With the presence of hypochlorite (OCl) compounds in the electrolyte without any electric current flowing, and with the low content of sodium dichromate (Na₂Cr₂O₇) compounds, the corrosion rate occurring on the electrode will increase drastically, especially on the cathode side [9].

Table 2. Sodium Chlorate Production in Change Flowrate Condition.

Day	Current (A/h)	Flowrate (liter/h)	Voltage (volt)	Resistance (ohm)	Product NaClO ₃ (kg/h)	Power (kWh)	MWh per ton NaClO ₃
Day 1	15.32	6.09	2.88	0.19	0.69	94.71	5.72
Day 2	16.04	6.46	2.91	0.18	0.71	99.96	5.83
Day 3	16.41	6.71	2.91	0.18	0.72	101.56	5.85
Day 4	17.14	6.91	2.97	0.17	0.74	109.34	6.14
Day 5	17.88	7.07	2.97	0.17	0.76	113.99	6.24
Day 6	18.03	7.21	2.99	0.16	0.79	115.16	6.09
Day 7	18.73	7.26	2.95	0.16	0.80	116.58	6.04
Day 8	19.44	7.69	3.04	0.16	0.86	123.77	5.99
Day 9	19.98	8.01	3.06	0.15	0.88	127.90	6.06

Shown in Table 2, on day 7 the voltage value of the cell electrolyzer system has decreased even though the product produced is higher. This is because on day 6 an acid wash process was carried out on both electrodes (trend graphic also can be seen in Figure 5). The decrease in voltage value indicates that the surface of the anode and cathode becomes clean again and free from all deposits of side reactions or rust particles from corrosion reactions, so that the electric current flowing is more optimal. With more sodium chlorate (NaClO₃) product, it can be seen on day 7 that the electrical energy consumption per ton of sodium chlorate (NaClO₃) is lower than the previous days which have a lower amount of sodium chlorate (NaClO₃) product. But on day 8

onwards, the value of the voltage cell electrolyzer system has increased again because the electrolysis process continues, and the amount of product sodium chlorate (NaClO_3) continues to increase. If the amount of product sodium chlorate (NaClO_3) is maintained as on day 7, then the increase in electrolyzer cell voltage will tend to slow down. Table 2 also shows that with higher sodium chlorate (NaClO_3) production compared to Table 1, the electrical energy consumption per ton of sodium chlorate (NaClO_3) is lower, average only 5.99 MWh compare with 6.15 MWh. Only on day 5 the electrical energy consumption per ton of sodium chlorate (NaClO_3) is higher. This condition happens due to the voltage value of the cell electrolyzer continues increase during the electrolysis process, so that more electric current is needed in the processes.

By increasing production capacity up to 58.24% in day 9 compare with average production capacity in Table 1, resistance value will decrease up to 31.25% and consumption electrical energy saving per ton sodium chlorate (NaClO_3) around 0,089 MWh. This value is become larger in industrial scale because mostly annual production of sodium chlorate (NaClO_3) to produce chlorine dioxide (ClO_2) above 100,000 ton (similar with annual saving power 8,900 MWh).

4 CONCLUSION

In the sodium chlorate (NaClO_3) production using the electrolysis process, keeping the electric current and flow rate in the cell electrolyzer system stable will produce a relatively stable product sodium chlorate (NaClO_3) as well. But this causes the voltage and resistance of the cell electrolyzer system to increase over the time and electrical energy consumption per ton of sodium chlorate (NaClO_3) will increase too. Altering the sodium chlorate (NaClO_3) production capacity can be used to maintain the power consumption by reducing resistance values. Performing an acid wash process in a certain period on the cell electrolyzer system is useful to keep the voltage value from continuing to increase due to the corrosion reaction process on the cathode and depositing on the anode during the electrolysis process. In the end, these two processes will reduce the total electrical energy consumption per ton of sodium chlorate (NaClO_3) produced and keep electrolysis process running well.

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