

OPERATING CONDITIONS EFFECTS OF AN ELECTRODIALYSIS MODULE ON HYDROCHLORIC ACID AND SODIUM HYDROXIDE FORMATION

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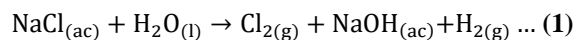
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ABSTRACT: Sodium hydroxide is produced mainly by the electrolysis of an aqueous solution of sodium chloride using mercury, diaphragm and membrane technologies. The membrane cell gained greater importance in recent years due to its environmental advantages and lower energy consumption. In this work, electrodialysis equipment has been built on a laboratory scale, using cation exchange membrane and anion exchange membrane, the effect of the operating conditions of the electrodialysis module on the concentration of hydrochloric acid and sodium hydroxide has been studied. The experimental results show that 15 volts are the most suitable operating condition, initial acid and base concentration of 0.05N and sodium chloride concentration of 50 g/L. reaching a hydrochloric acid concentration of 0.22N and 0.25N of sodium hydroxide, respectively, during 210 minutes of operation of the electrodialysis module. The energy consumption was 14.9kWh/Kg of sodium hydroxide and the current efficiency of 53.5%. The process offers the advantage of using clean technology compared to traditional processes for acid and base production.

Keywords: Electrodialysis, Bipolar electrodialysis, Electromembrane, Hydrochloric acid, Sodium hydroxide

1. INTRODUCTION

Inorganic products such as hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid and sodium hydroxide are indispensable in many industrial processes, such as fertilizers, steelmaking, water treatment, etc. As the development of the industry increase, the consumption of these chemicals must increase in the future. The chlorine-alkali industry produces chlorine, sodium hydroxide and hydrogen by electrolysis of NaCl aqueous solutions as indicated in the following chemical equation:



At present, the chlor-alkali process is mainly represented by three technologies; mercury cell, diaphragm and membrane cell. The main difference between these technologies is cell configuration and the use of different materials. According to Fig. N° 1, a general scheme of the chlor-alkali process is shown.

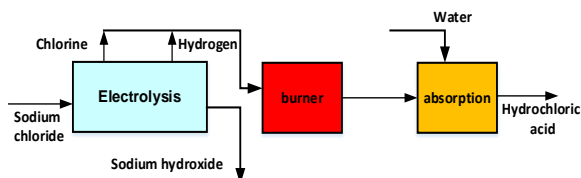


Fig. N° 1 NaOH and HCl production

According to the diagram, sodium hydroxide is produced at the electrolysis stage, however, to produce hydrochloric acids other traditional operations are needed, such as a combustion furnace and absorption column. In these traditional processes, mercury and asbestos emissions occur. This has led to the search for new alternatives to eliminate these stages of the traditional process.

Electrodialysis is a process of separation of ionic species from aqueous solutions, based on the selective migration of ions through ion exchange membranes under the influence of a direct current electric field. These processes generally contain two types of ion exchange membranes; anionic membranes (MA) selectively permeable to anions and cationic membranes (MC) which are selective to cations, placed alternately and separated by expansion joints between two electrodes.

When an electric potential is applied to the electrodes, the migration of ions to the electrodes with opposite charge begins. The cations penetrate the cationic membranes, but these are blocked by the anionic membrane. Similarly, the anions penetrate the anionic membranes but the anionic membranes block the anions. The process at the end results in increasing the concentration in one of the compartments and dilution in another compartment. Inorganic and organic sales found in effluents, such as sodium

chloride, sodium sulfate, sodium nitrate, sodium acetate, etc., can become its parameters and bases due to bipolar electrodialysis.

The ion exchange membranes can take different possible configurations forming cells of two or more compartments, each of these configurations can have various possible applications, such as desalination of brackish water, demineralization of wine, the formation of hydrochloric acid and sodium hydroxide, etc. The purpose of this investigation is, first, to obtain NaOH and HCl by electrodialysis instead of NaOH, Cl₂, H₂ and second, to carry out a study of the influence of the operation variables such as initial acid concentration, base concentration of sodium chloride and electric potential on the final acid concentration and base concentration, in addition to the process efficiency and energy consumption, the latter is fundamental to understand the process economy and scalability.

2. MATERIALS AND METHODS

2.1. Materials

Both analytical grade reagents such as Na₂SO₄, NaCl, NaOH y HCl and deionized water produced by EDI equipment were used throughout the experience. The acid and base solutions were generated using feed solutions consisting of 0,01, 0,025 and 0,05 N of hydrochloric acid and sodium hydroxide, 5, 20 and 50 g/L NaCl and applied a voltage of 5-15. Volts maintaining a constant concentration of 0,05M H₂SO₄.

2.2. Membranes

Two commercial membrane classes were selected in this work, from the company FuMA-Tech GumbH, Germany.

Table 1 Membrane characteristics

| Membrane Characteristics | Cationic Membrane (FTCM-E) | Anionic Membrane (FTAM-E) |
|--|----------------------------|---------------------------|
| - Electric resistance (Ω/cm ²) | 2,5- 3,5 | 2,5- 3,5 |
| -Exchange capacity (meq/g) | 1,5 - 1,8 | 1,4 - 1,7 |
| -Thickness (mm) | 0,17 - 0,19 | 0,16 - 0,18 |

2.3. Membrane Configuration

Figure N°2 shows the configuration of the membranes, one anionic and two cation exchange membranes placed between the cathode and the anode.

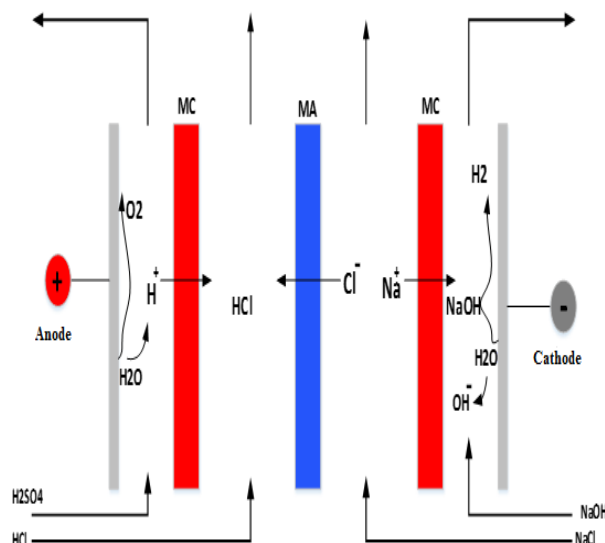


Fig. 2 Membrane Configuration

2.4. Electrodialysis Equipment

The cell built was a press filter type laboratory scale with four compartments, it was built with acrylic material on which three membranes were assembled with their respective turbulence promoters, and secured with 8 transverse bars with nuts to prevent any type of leakage, mixed or spilled liquid.

Two acrylic plates with two inlets and two outlets at the end disposed of for the flow of salt and hydrochloric acid solutions. Two 1.5 cm thick acrylic frames, where two electrodes (of 100 cm² effective area) are inserted, made of steel and platinum titanium, each acrylic plate contains an inlet and outlet through which passes the sodium hydroxide solution and the diluted solution of sulfuric acid. The dimension of each membrane is 10 cm × 9 cm.

All experiments were performed in a batch mode at room temperature. The acid, base and salt solutions were recirculated by pumps independently, the flow rate was regulated by a stepped valve. The initial volume of solutions in each compartment was 500 ml. The voltage and current were recorded directly from the electrical source. The time used for each experiment was 21 seconds.

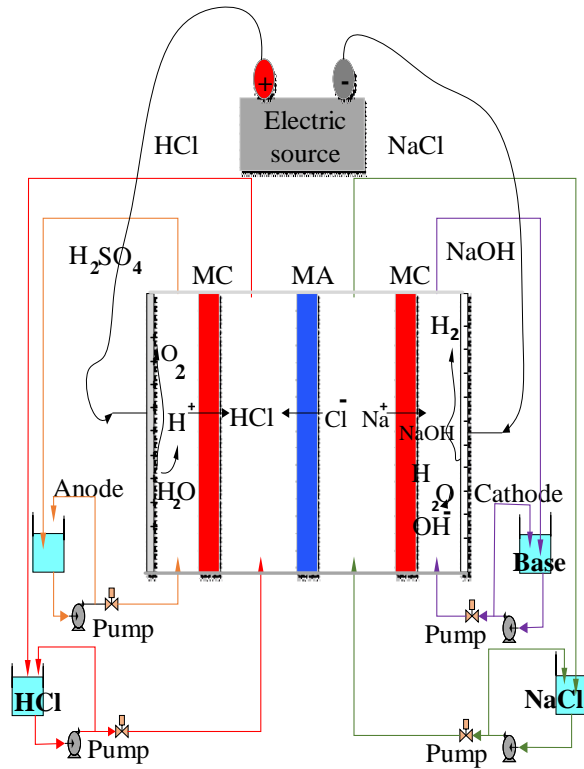


Fig. 3 Experimental equipment

2.5. Analytical Methods

The concentrations of NaOH and HCl formed were determined by titration with a standard concentration of 0,01 mol/L of hydrochloric acid and sodium hydroxide. The chloride ions by titration of 0,01N silver nitrate. The conductivity was measured using an ADWA AD 330 Conductimeter and the pH in the acid and base compartment was measured by ADWA Switzerland pH meter.

2.6. Process Indicators and Electrodialysis

2.6.1. Separation percentage

The separation percentage is evaluated by Eq.(1). The concentration or conductivity is measured at the beginning and then at a certain time.

$$S = \left(\frac{C_{t=0} - C_{t=t}}{C_{t=0}} \right) \times 100\% \dots \dots \dots (2)$$

2.6.2. Base acid concentration

Changes in the concentration of hydrochloric acid and sodium hydroxide were determined by titration using phenolphthalein as an indicator. The concentration is calculated using the following equations (4)

$$C_{HCl} = \frac{C_{NaOH} \times V_{NaOH}}{V_{HCl}} \dots \dots \dots (3)$$

$$C_{NaOH} = \frac{C_{HCl} \times V_{HCl}}{V_{NaOH}} \dots \dots \dots (4)$$

HCl, NaOH mol/L; V_{HCl} , V_{NaOH} (liters).

2.6.3. Efficiency electric current

The current efficiency (η) for a specific product is an important critical parameter to assess the viability of ED since it determines the applied current fraction that is effectively converted.

$$\eta = \frac{zF(C_f - C_i)V_t}{N \int_0^t i dt} \times 100\% \dots \dots \dots (5)$$

η : current efficiency; Faraday constant (96500A.s/mol), C_f y C_i - initial and final concentration of HCl solution (mol/m³); i , electric current intensity (A) and N , number of cell pairs. V_t volume of recirculated HCl solution

2.6.4. Energy consumption

The energy consumption was determined by the Eq. (3)

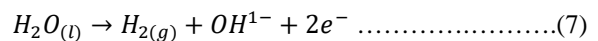
$$E = \frac{V \int i dt}{C_t V_t P \cdot F} \dots \dots \dots (6)$$

Where: E (Kwh/kg) is the required energy consumption to form the acid and base, i (t) electric current, V is the cell potential difference t : time V_t : volume (m³) as a function of time, HCl solution final concentration mol/m³.

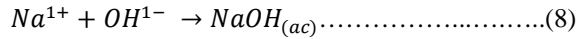
3. RESULTS AND ANALYSIS

3.1. pH Evolution in the Acid and Base Compartment

Figures 4 and 5 show the pH changes in the compartments of both sodium hydroxide formation and hydrochloric acid, the graphs tendency is explained in terms of the chemical reactions. In the base compartment, water is decomposed by electric current producing hydroxyl ions and hydrogen gas as indicated in the following equation:



The sodium ions of the sodium chloride compartment are permeable to the cathode through the cation exchange membrane forming sodium hydroxide together with the oxydryl ions as indicated the equation:



The pH in this compartment increases over time due to the formation of oxydryl ions, sodium ions and sodium hydroxide concentration formed as a function of time. Figure 4 shows the pH increases more quickly when a voltage of 15 volts is applied. Regardless of the initial concentration of NaOH in the range of 0,01 and 0,05 N.

In the acid compartment, the hydronium ions produced at the anode are permeable by the cationic membrane and combined with the chloride ions which are permeable by the anionic membrane forming hydrochloric acid according to the following reaction:

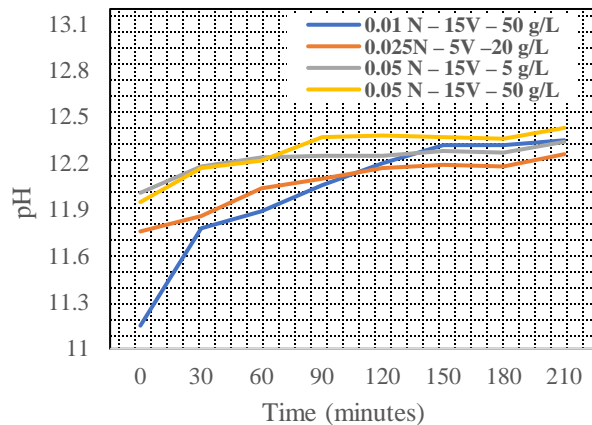
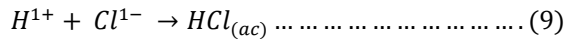


Fig.4 pH dependence in the base compartment

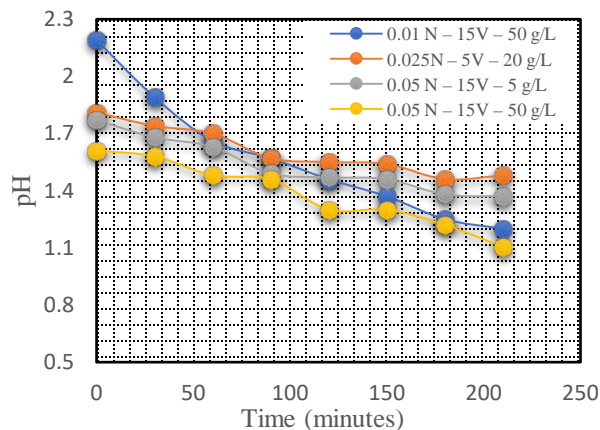


Fig.5 pH dependence in the acid compartment

Figure N°5 shows that pH decreases rapidly when a voltage of 15 volts is applied.

3.2. Evolution of the Acid and Sodium Hydroxide Concentration

Figure 6 and 7 show the increase in the acid and base concentration is more significant when a voltage of 15 V is applied and it is more significant for the acid when the initial concentration is 0,05 N. The hydrochloric acid concentration reached is 0,22 N and sodium hydroxide 0,25 N for initial contractions of 0,05 N at 15 volts.

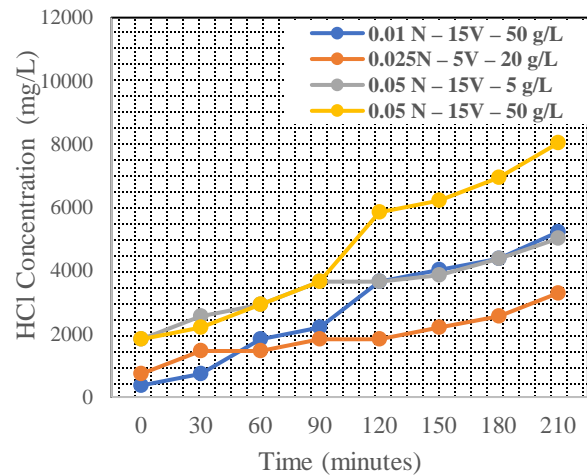


Fig.6 Changes of HCl (mg / L) concentration

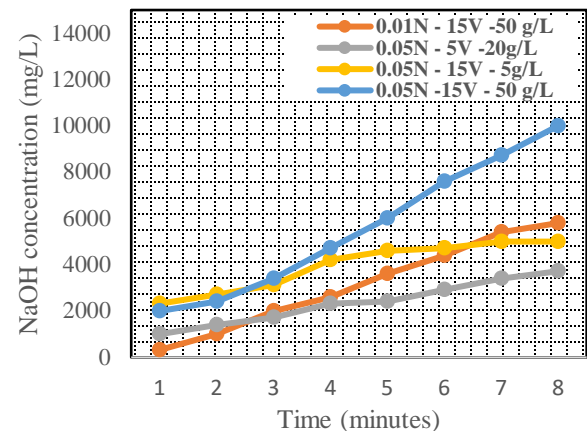


Fig.7 Changes of NaOH (mg / L) concentration

3.3. Change in Conductivity of Base Acid

Figures 8 and 9 show that the conductivity trend grows over time for both the acid and the base, the acid

conductivity grows faster than the base reaching 63,5 mS/cm, with a voltage of 15 volts for the base of 35,2 mS/cm.

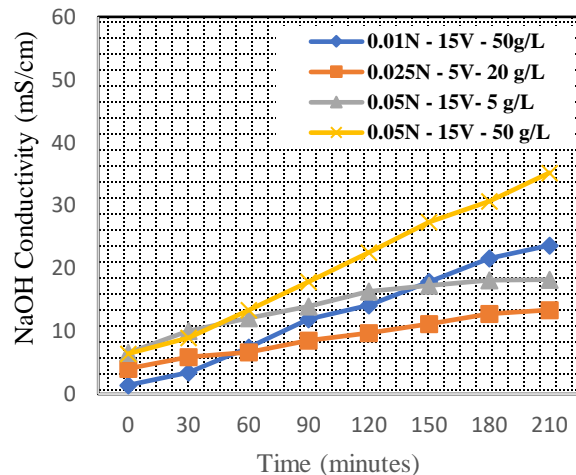


Fig.8 Change of NaOH Conductivity

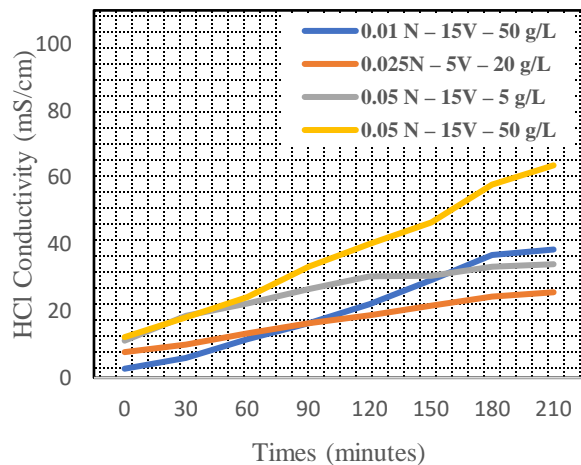


Fig.9 Change of HCl Conductivity

3.4. Variation of Conductivity of NaCl

In the sodium chloride compartment, a gradual decrease in conductivity is observed as a function of time, which is the result of the diffusion of sodium ions by the cationic membrane and the chloride ions that are permeable through the anionic membrane.

Figure 10 shows that the conductivity of sodium chloride decreases, and at Eq.(2) the separation percentages have been evaluated at an applied voltage of 15 volts, obtaining 19,3% when the concentration of sodium chloride is 50g/L and 95,28% when the concentration of sodium chloride is 5g/L.

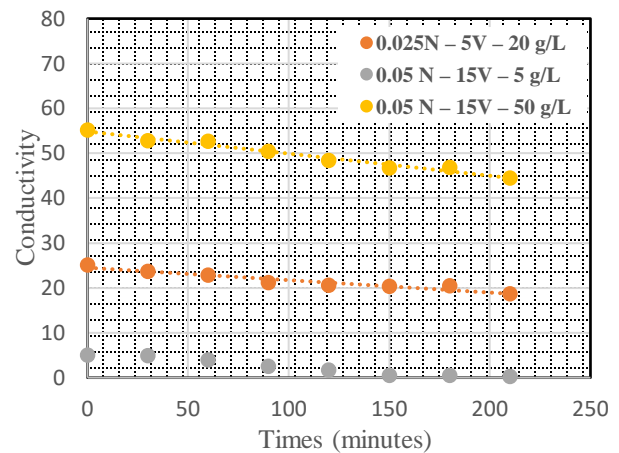
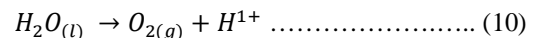


Fig.10 Changes of NaCl Conductivity (mS/cm)

3.5. Conductivity Evolution of Sulfuric Acid

In this compartment, water decomposes into hydronium ions and oxygen ions due to the action of electric current as indicated the equation:



In the first ionization stage, the sulfuric acid in aqueous solution produces hydronium ions

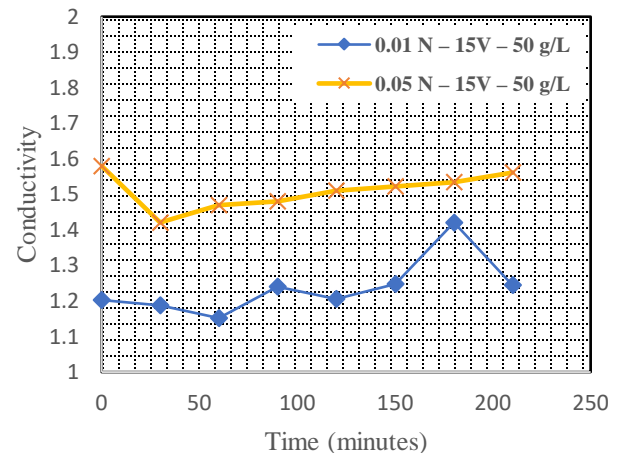


Fig. 11 Changes of sulfuric acid (mS/cm) conductivity

Simultaneously hydronium ions are permeable by the cationic membrane to the acid compartment. As expected, the conductivity and contraction of sulfuric acid in this compartment varied slightly throughout the experiment, as indicated in figure 11, due to the formation and disappearance of hydronium ions, independently of the applied electrical voltage.

3.6. Effect of Initial Concentration of Hydrochloric Acid and Sodium Hydroxide

To determine the evolution of initial concentrations of HCl and NaOH it was necessary to work with two initial concentrations of NaCl (20g/L and 50g/L) and two different electrical voltage (10 V and 15V). The acid and base initial concentrations were 0,01N, 0,02N and 0,05N.

Considering 50g/L of NaCl as initial concentration, figure 12 shows the best result to 0,05N initial concentration of acid when a voltage of 10v is applied reached 0,14N and 0,22N when a voltage of 15 V is applied. At the same figure, NaOH initial concentration is 0,05N and reached a final concentration of 0,22N when a voltage of 10v is applied, and 0,25N when a voltage of 15v is applied.

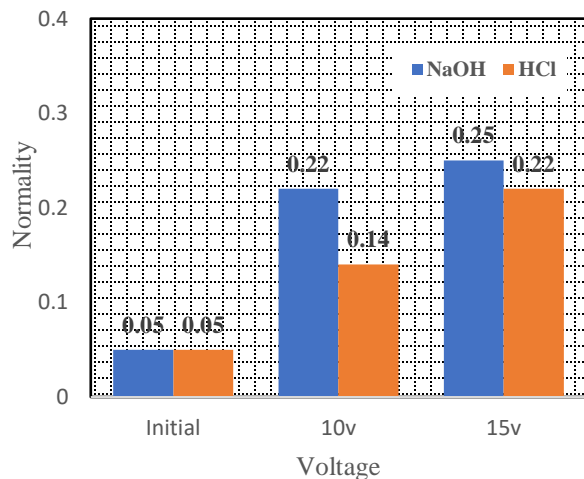


Fig.12 Evolution of normal concentration of HCl and NaOH

3.7. Effect of Applied Electrical Voltage

Figure 6 and figure 7 show that, when the module worked with a voltage of 15 volts, it was possible to obtain the highest concentration of acid (8030mg/L – 0,22 N) and base (10000mg/L – 0,25 N) at initial concentrations of HCl (1825 mg/L- 0,05 N) and NaOH (2 000 mg/L -0,050 N) using 50 g / L of NaCl.

Equations 5 and 6 have evaluated the specific energy consumption, obtaining 14,9 kWh / Kg of NaOH, and the current efficiency was 53,5% at the most adequate operating conditions of the electrodialysis equipment.

4. CONCLUSIONS

Electrodialysis (ED) represents a method of separating chloride anions, sodium cations from a

sodium chloride model solution and simultaneously obtaining aqueous solutions of hydrochloric acid and sodium hydroxide in different compartments.

ED with ionic membranes offers a clean technology, compared to traditional processes for the production of acid and base. In this study, it was shown that according to the sodium chloride feed concentration, the applied voltage and the initial concentration of the acid and base, the results show that when the applied voltage is 15 volts, the initial concentration of the acid and base is 0,05N and 50 g/L of NaCl an acid concentration 0,22N and 0,25N of sodium hydroxide is reached.

5. Acknowledgments

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