

Wallace & Tiernan[®] Basic Principles of Electrochlorination

A review of the factors affecting chlorine generation efficiency.

Paper 1

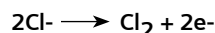
Introduction

On Site Electrolytic Chlorination

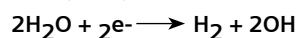
Electrochlorination is the name given to the process whereby an electrical current is used to convert sodium chloride solution to sodium hypochlorite or chlorine.

In a basic cell an electric current is passed through a sodium chloride brine via an anode and cathode.

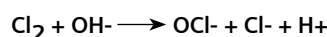
At the anode the chloride ions are oxidised (electrons removed) to form chlorine (Cl₂).



At the cathode water is reduced (electrons added) to form hydrogen and hydroxyl ions.



In an open reactor the electro-generated species are free to mix and react.



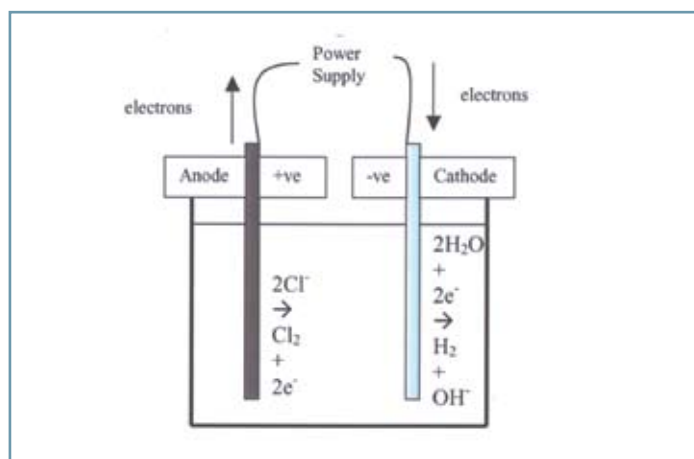
In a divided reactor a membrane prevents the free mixing of the electrode products while still allowing a current to pass. The divided reactor may be configured to produce chlorine gas, sodium hydroxide and hydrogen or the sodium hydroxide and chlorine

may be recombined to form sodium hypochlorite outside the reactor.

In practice a number of electrodes are normally connected together to form an electrolyser assembly. They may be arranged as a mono-polar assembly where each electrode is either an anode or cathode or in a bi-polar arrangement where part of each electrode serves as a cathode and part as an anode.

The Anodic Reaction

The reaction of chloride ion to chlorine gas ($2\text{Cl}^- \longrightarrow 2\text{e}^- + \text{Cl}_2$) is not the thermodynamically preferred reaction at an anode in brine solution. Normally the oxidation of water to oxygen and hydrogen ion ($2\text{H}_2\text{O} \longrightarrow 4\text{e}^- + \text{O}_2 + 4\text{H}^+$) is predominant. In order to obtain a reasonable yield of chlorine with a minimal oxygen content it is necessary to use a catalyst which promotes chlorine production whilst inhibiting oxygen evolution. Typically, an anodic coating containing precious metal oxide is used to achieve the maximum efficiency of chlorine evolution. A ruthenium dioxide containing coating in combination with other precious metals and valve metal oxides applied to a titanium substrate is generally used to maximise the efficiency of chlorine generation while, at the same time, providing stability at an economical cost. This type of electrode is often referred to as a DSA[®] (dimensionally stable anode). The catalytic effect of the ruthenium dioxide causes a lowering of the potential (Voltage) needed to cause the chlorine evolution reaction to happen at a reasonably fast rate. The difference between the theoretical potential at which the reaction should take place and the actual potential found to be necessary for practical generation is called the "overpotential".



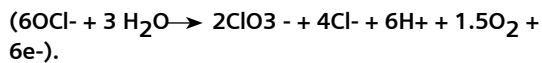
Product Sheet

An effective catalytic coating is said to reduce the overpotential for chlorine generation.

The performance of catalytic anodes for chlorine generation is strongly affected by temperature. Temperatures above 37 - 40°C (98 - 104°F) may favour oxygen generation, especially at chlorine concentrations above 0.6% wt., whereas temperatures less than 10°C may result in loss of coating as well as a significant increase in oxygen production. Catalytic coatings have been developed specifically for certain operating conditions.

In spite of the improvement offered by the DSA there will still be a small amount of oxygen generated from water oxidation.

In addition to this a portion of the hypochlorite generated will be oxidised at the anode to chlorate.



The rate of hypochlorite oxidation at the anode is a function of the concentration of hypochlorite and temperature. This oxidation is partly responsible for the inherent limits to the efficiency of a mixed cell electrochlorinator.

The Cathodic Reaction

The main cathodic reaction is the reduction of water to hydrogen and hydroxide. The efficiency of the electrochlorination process is partly dependent on the electrical potential (Volts) required for hydrogen evolution at the cathode. Different metals exhibit a different "cathodic hydrogen overpotential". For example, Hastalloy C has a lower overpotential for hydrogen than titanium and utilises less power (Current x Voltage) per unit of chlorine generated. Coatings of precious metals have been shown to improve the generation efficiency by up to 10%.

The second cathodic reaction of significance is the reduction of hypochlorite back to chloride, ($\text{OCl}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$).

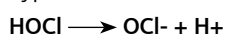
This reaction is limited by the concentration of hypochlorite in the electrolyte. That is to say that rate of loss of hypochlorite is proportional to the concentration of hypochlorite. The effect of this reaction increases with electrolysis time. This is the major factor influencing the potential salt and power efficiency and maximum hypochlorite concentration obtainable from an undivided electrochlorinator.

A further cathodic reaction is the reduction of oxygen to water, ($\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$).

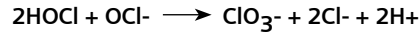
This is insignificant in a normal electro-chlorination plant but would use less energy if a suitable catalyst could be found. In addition the process would not produce hydrogen.

Reactions in the electrolyte solution

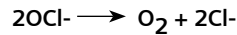
The products of the reactions at the anode and cathode are free to react in the electrolyser. The main reaction is that between the elemental chlorine and the hydroxide to form hypochlorite. There is also the dissociation of hypochlorous acid:



And the reaction of the hypochlorous acid and hypochlorite ion to form chlorate:



In addition to this is the decomposition of hypochlorite to oxygen:



Chlorine generation efficiency - Current efficiency

Faraday's Law of Electrolysis relates the amount of electricity to the amount of electrochemical product formed or consumed. If we consider a simple electrochemical cell as in Figure 1., the amount of electricity (number of electrons) equates to the amount of chemical change at the anode and cathode. The current (Amps) is a measure of the rate of the chemical reactions at the electrodes.

This is expressed as: $Q = mnF$

Where:

Q = electrical charge in Coulombs

m = amount of reactant consumed or product formed (in Moles)

n = number of electrons required to convert reactant to product

F = Faraday's constant (96484 coulombs / mole)

So for the generation of chlorine in a mixed cell electrolyser the overall reaction of interest is:



One Molecule of chlorine requires 2 electrons transferred.

The electrical charge required to generate one Mole (71g) is:

$$1 \times 2 \times 96484 = 192968 \text{ Coulombs}$$

$$1 \text{ Ampere} = 1 \text{ Coulomb / second or}$$

$$Q = I dt \text{ Or under constant current: } Q = It$$

The current efficiency is a measure of the ratio of the theoretical amount of current required by the reaction being considered to the amount of current actually consumed.

Current efficiency = charge consumed in reaction of interest / total charge passed.

The typical current efficiency of an undivided electrochlorination cell is approximately 60% at a hypochlorite concentration of about 8000 mg/l. The current efficiency rises to 80 - 90% at hypochlorite concentrations between 1000 - 2000 mg/l.

This can be demonstrated for an 8000 mg/l hypochlorite generator as follows:

An electrolyser consisting of 4 cells generates 71.4 kg / day equivalent chlorine.

It requires uses a current of 952 A which multiplied by 4 cells gives a total effective current of 3808 A.

From Faraday's Law 71.4 kg divided by 0.071 kg gives 1006 moles.

$$1 \times 2 \times 96484 = 1.93 \times 10^5 \text{ Coulombs}$$

$$1006 \times 1.94 \times 10^5 / (24 \times 60 \times 60) = \text{Amps} = 2259$$

So current efficiency = 2259 / 3808 = 59%.

The lost current is that which is consumed in creating unwanted reaction products. In this case these will be the back reduction of hypochlorite to chloride at the cathode

and the creation of chlorates and oxygen at the anode. The potential for lowering the effect of cathodic reduction of hypochlorite is very limited in a mixed cell electrochlorinator. The options of reducing the cathode area relative to the anode area and of coating the cathode with a thin porous ceramic coating have been investigated but with limited success. The back-reduction effect can be almost entirely removed if an ion exchange membrane is utilised.

Chlorine generation efficiency - Power efficiency

Current efficiency is actually of little benefit in making an economic assessment of an electro-chlorination plant. Electrical energy is normally paid for in units of kW hours. 1 kW = 1000 J / second so 1 kW hour = 1000 x 3600 = 3.6 M Joule.

To calculate electrical power (P) requires a knowledge of the Voltage (V) and the Current (I).

$$P = IV \text{ And } V = IR \quad \text{So } P = I^2R$$

The power for an electrochlorination plant is easily calculated from the Voltage and Current supplied to the electrolyser. This is the DC power. The AC power is the actual power consumed by the whole plant. The AC consumption is always higher than the DC consumption. The main reason for this is the efficiency of the power supply.

Referring back to the example above the power efficiency can be calculated. This is normally quoted in units of kW hour / kg.

So, for the example 71.4 kg / day requires 2236 A at 15 V.

$$\text{So, } P = 952 \times 15 = 14280 \text{ W or } 14.28 \text{ kW}$$

For 24 hours this equates to:

$$14.28 \times 24 = 342.72$$

$$342.72 / 71.4 = 4.8 \text{ kW hour / kg Cl}_2$$

We have shown that the current is a function of the current efficiency, which is largely related to the rates of reaction of the various chemical species in the reactor. The voltage is a function of a number of variables, which may be varied to enhance the overall efficiency.

The major contributor to the cell voltage is the energy barrier required to break down the chloride at the anode and the water at the cathode. This is known as the decomposition potential and is largely fixed by the thermodynamic properties of the chemicals involved. Part of the decomposition potential is, however, due to the properties of the anode and the cathode namely the overpotential, which has been previously referred to. Improvements to the coatings of both the anode and the cathode may improve the efficiency of the electrolyser.

A further factor affecting the cell voltage is the electrical resistance. As $V = IR$ the component most amenable to change is likely to be the resistance of the electrochemical reactor.

Resistance in an undivided electro-chlorinator may be due to the following factors:

1. Electrical connections to the electrode plates
2. Concentration of sodium chloride in the brine
3. Temperature of the brine
4. Volume of hydrogen bubbles in the brine
5. Distance between the electrodes
6. Surface area of the electrodes

1. Electrical connections

The resistance of the connections to the electrode assembly may have a significant effect on the voltage necessary to maintain the operating current. Copper connections must be of sufficient cross section to carry the current without heating and connections between the wire or bus-bar and the electrode assembly may need to be optimised with conductive paste and/ or compression.

2. Concentration of sodium chloride

The resistance of the brine decreases linearly with increasing concentration. The specific conductance of a solution is obtained from the formula:

$$k = l / AR \text{ where:}$$

$$k = \text{specific conductance (ohm}^{-1} \text{ cm}^{-1})$$

$$l = \text{length (cm)}$$

$$A = \text{area (cm}^2)$$

$$R = \text{resistance (ohms)}$$

If we know the specific conductance of the brine concentration being used at the temperature in the electrolyser then it is possible to calculate the resistance between the anode and cathode in each cell.

$$R = l / kA$$

3. Temperature

The resistance of the brine decreases as the temperature increases.

4. Hydrogen

The presence of hydrogen evolved from the cathode results in non-conducting zones in the electrolyte. The effect may be controlled by the flow and fluid circulation in the cell which is mainly influenced by the geometry of the electrode arrangement. Generally the closer the electrodes the greater the increase in resistance due to trapped bubbles. Increasing the gap allows the bubbles to be released. The height of the electrodes is also significant, as the hydrogen bubbles tend to coalesce as they rise.

5. Inter-electrode gap

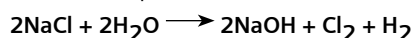
The electrical resistance increases linearly with the distance between the electrodes. (See 2. Above.)

6. Electrode surface area

The resistance is a function of the area of the electrodes. (See 2. Above.)

Chlorine Generation Efficiency - Salt efficiency

The cost of salt may be the most significant factor when assessing the economic viability of an electro-chlorination plant. The best salt efficiencies in a mixed cell electrolyser are obtained with the lower concentrations of salt, typically of 2.6 - 3.0% wt., and lower hypochlorite concentration of less than 8500 mg/l. If the salt efficiency was 100% then 2 moles of salt would make 1 mole of chlorine equivalent according to the overall equation for electro-chlorination:



The mass of 2 moles of sodium chloride is $2 \times 58.5\text{g} = 117\text{g}$

1 mole of chlorine is 71g

In terms of weight (mass) the ratio would be $117/71 = 1.65 \text{ kg salt / kg chlorine.}$

Under normal operating conditions a mixed cell

electrochlorination plant will run at between 3 - 3.9 kg / kg Cl₂.

A divided electrolyser may operate nearer to 100% salt conversion efficiency. The OSEC®-NT operates at 1.7 kg salt / kg Cl₂.

The best salt efficiencies in a mixed cell electrolyser are obtained with the lower concentrations of salt. This is largely due to the lowering of the back-reduction of hypochlorite at lower hypochlorite concentrations. It is possible to alter the concentration of brine along the length of an electrolyser. This may be achieved by dosing brine and dilution water at the front end of the electrolyser and then injecting more dilution water further down.



Summary

The design of an efficient electro-chlorinator will take all of the above factors into account to produce the optimum solution. Good engineering practice will ensure that electrical joints have the highest conductivity and that anode coatings suited to the operating environment are selected. The inter-electrode gap will be determined by a trade off between solution resistance and hydrogen release.

Temperature can be controlled to the optimum value by diverting heat from the final product via a heat exchanger to ensure that the brine entering the electrolyser is at a high enough temperature.

The salt conversion efficiency may be optimised by maintaining a sufficient dilution level to minimise the back reduction of the hypochlorite. This dilution also

ensures that the power to chlorine ratio is optimised.

The increase in economic generation efficiency resulting from increasing the dilution factor should be considered against the potential costs of operating at lower chlorine concentrations. These will include the requirements for larger storage tanks and dosing pumps.

Salt Conversion Efficiency

The salt conversion may be improved by operating the electrochlorination plant at lower brine dilution ratios. Laboratory experiments have shown that the optimum salt conversion value for OSEC® using a variety of different anode coatings is obtained with a brine dilution of 15:1 rather than the commonly used ratio of 10:1. The cost of improving salt conversion efficiency by dilution is a lower hypochlorite strength.

Current Efficiency

Electrical power efficiency may be optimised by reducing brine concentration below the normal operating dilution of 10:1. As for salt efficiency this appears to reach an optimum at a dilution ratio of 15:1.

Power Efficiency

Membrane divided electrolysers have the potential for improvements to electro-chlorination efficiency. Back reduction of hypochlorite is effectively prevented thereby increasing salt efficiency dramatically. The perfluorocarbon ion exchange membrane used will increase the resistance between the anode and cathode so the operating voltage must be higher with a consequent increase in power requirement. However this may be more than offset by the increased Faraday efficiency due to the prevention of hypochlorite back-reduction.

The economics of electrochlorination is strongly influenced by local conditions and requirements. For example, if salt is relatively inexpensive then salt conversion efficiency becomes less significant. Likewise, if the hypochlorite product strength is not a critical factor then both salt and power efficiency can be improved.

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