

Electrolyzed Oxidizing Water Generation Methods

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Electrolyzed oxidizing (EO) water, also known as Denkaisui in Japan, or electro-chemically activated water (ECA or ECAW), is a solution generated by passing a dilute salt solution (NaCl and KCl are commonly used) through an electrolytic cell. The anode side of an electrolytic cell, from which acidic EO water is obtained, produces various chlorine compounds and ions such as hypochlorous acid (HOCl), hypochlorite ion (OCl⁻) and chlorine gas (Cl₂), which are all collectively known as free chlorine. HOCl is the main antimicrobial agent present in EO water. EO water generally has a low pH (2.3 – 2.7) and a high oxidation – reduction potential (ORP) (> 1000 mV).

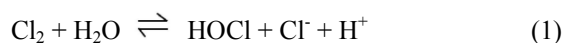
On the cathode side of the electrolytic cell, a dilute solution of NaOH is generated, and this is sometimes referred to as electrolyzed reducing (ER) water. Unlike EO water, the principal use of ER water is not in the reduction of microbial numbers. Instead, ER water is mainly used as a degreaser and cleanser¹. Additionally, work has been done on the health benefits of ER water in terms of cancer prevention, wound care, skin care and also as drinking water for improving digestion and cow milk production². Chemically, ER water is characterized as having a high pH (10-11.5) and a low ORP (-800 to -900 mV)³.

Properties of EO water

EO water is primarily a solution consisting of HOCl, OCl⁻, and dissolved Cl₂, that when in contact with organic materials, variable amounts of organic chlorides, such as trihalomethanes (THMs), chloramines and haloacetic acids (HAAs), all often referred to as bound (or combined) chlorine, are formed. The sum total of HOCl, OCl⁻, Cl₂, and chloramines is known as the total chlorine concentration of an EO water solution.

Ultimately, the concentration and ratio of the species of free chlorine, combined chlorine and chloride ion are dependent on method of generation, and pH of EO water.

In its pure form, chlorine (Cl₂) is a poisonous yellow-green gas. However, chlorine exhibits a pH-dependent chemistry. In other words, the pH of the solution that chlorine is dissolved in will play a dominant role in what compound chlorine will assume. From pH 3 to 7, HOCl is the dominant chlorine species. HOCl is a strong oxidant (ORP > 900 mV), and is the preferred free chlorine species for disinfection. HOCl is generated by the hydrolysis of dissolved Cl₂, as demonstrated in the following equation:



Due to the high molar concentration of water in aqueous solutions, this reaction proceeds via 1st order kinetics ($k_1 = 22.3\text{s}^{-1}$)⁴. Disregarding the effects of all other factors (i.e. product concentrations, temperature, catalysts), the concentration of Cl₂ is the most important factor in determining forward reaction rate in equation 1.

Below pH 3, Cl₂ becomes increasingly dominant. One major cause of free chlorine loss from water at low pH (< 4) is due to off-gassing of Cl₂. The solubility of chlorine gas at 20°C is about 7g/l pure water, and it is reasonable to assume that this solubility can be altered by temperature changes and changes in partial pressure over the surface of the liquid (as Henry's Law states). At low pHs, the reverse reaction of equation 1 predominates, and it is a 3rd order reaction ($k_{-1} = 4.3 \times 10^4 \text{ M}^{-2}\text{s}^{-1}$)⁴. As evident, this reaction proceeds at a much greater rate than the forward reaction described previously. However, it is important to understand that since this reaction relies on the availability of free protons and hypochlorous acid, a low pH is necessary to shift the

equilibrium to the left in equation 1. A low pH is necessary for this because both hypochlorous acid and free protons exist in greater quantities at low pH, thereby increasing the likelihood of the simultaneous collision of the three species required for the reverse reaction in equation 1 to predominate.

Above pH 7.54 (the pKa of HOCl at room temperature), OCl⁻ is the dominant free chlorine species. OCl⁻ is not as strong an oxidant as HOCl is (ORP ~ 600-700 mV), but it is more chemically stable. The pKa of HOCl can be determined experimentally using a variety of methods and the Henderson-Hasselbalch equation below:

$$\text{pH} = \text{pKa} + \log \left(\frac{[\text{OCl}^-]}{[\text{HOCl}]} \right) \quad (2)$$

At pH 7.54 (at 25°C), 50% of HOCl is deprotonated to OCl⁻. Therefore, above pH 7.54, the dominant chlorine species is OCl⁻.

The relative distribution of the three forms of free chlorine as they relate to pH can be visualized on Figure 1⁵⁾.

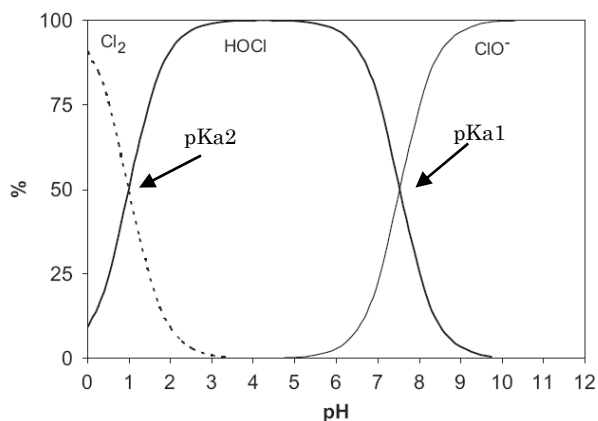


Fig. 1. Distribution of chlorine species from pH 0 to 12
Adapted from Deborde and vonGunten's review (2008).

Figure 1 assumes a chloride concentration of 5 mM. The label "pKa1" on the graph denotes the pKa of the OCl⁻ / HOCl couple. This pKa does not appear to be concentration dependent, but it is pH dependent. The "pKa2" label denotes the apparent pKa of the Cl₂ / HOCl couple. Unlike pKa1, pKa2 appears to shift based on chloride concentration. To be more specific, pKa2 will increase with increasing chloride concentration⁶⁾. According to the graph, the dominant free chlorine

species below pH 1 is Cl₂. The dominant species between pH 1 and 7.5 is HOCl, and the dominant species above pH 7.5 is ClO⁻.

Standard reduction potential is a measure of how easily a chemical species acquires electrons, becoming reduced in the process and oxidizing the species the electrons were acquired from. The larger and more positive the number is, the greater ability as an oxidant the species has. However, OCl⁻ has a standard reduction potential of 0.9 V, and HOCl has a standard reduction potential of 1.49 V, making HOCl a stronger oxidant than OCl⁻ is⁷⁾.

Electrochemical reactions within an EO water generator cause the formation of the chlorine species observed in EO water. The reactions in an EO water generator can be divided into 2 different categories: electrode localized reaction and reactions in solution.

Principle of EO water generation

Electrode localized reactions

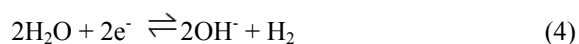
Electrode localized reactions are simply reactions that occur in the double layer region surrounding electrodes. The double layer region consists of specifically-adsorbed ions (the inner Helmholtz plane) followed by a layer of solvated ions (the outer Helmholtz plane). In terms of EO water generators, the reactions can be divided into two different types of reactions: an oxidation of chloride ion at the anode and a reduction of water at the cathode.

The anode side of an electrolytic cell, from which EO water is obtained, carries out the following reaction:



Electrons are abstracted from chloride ions (Cl⁻) in water by the anode to form chlorine gas.

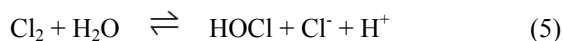
As mentioned previously, a dilute solution of NaOH is generated on the cathode side of an electrolytic cell used in EO water production. The following reactions occur in the cathode side:



Water is reduced at the cathode to form hydrogen gas and hydroxide ions in (4). In contrast to EO water, ER water is characterized by a high pH (10-11.5) and a low ORP (-800 to -900 mV)³⁾.

Reactions in solution

Besides the solvation of chloride compounds in the feed solution, there are other chemical reactions occurring in solution which play an important role in the function of an EO water generator. The solution reactions in EO water are dependent on the electrode-localized reactions.



Dissolved chlorine gas either leaves solution or undergoes a rapid reaction with water to form hypochlorous acid (HOCl), protons and more chloride ions, as shown in (5). In (6), HOCl can lose a proton to form its conjugate base hypochlorite (OCl⁻) in a pH – dependent equilibrium.

Other reactions also occur in solution, and these reactions may contribute to the unique properties of EO water, despite being low in concentration. Like the primary reactions, these reactions are pH-dependent as well. Many of these reactions are involved in the slow decomposition of HOCl. For example, in the pH range of 5-8, the mechanism proposed by Adam *et al.*⁸⁾ involves the synthesis of chlorate (ClO₃⁻) from HOCl. These findings support much earlier work done by Lister⁹⁾. The decomposition of HOCl to ClO₃⁻ is third order, and the values of ΔH* and ΔS* are 64.0 ± 0.6 kJ / mol and -67.0 ± 2 J / mol K respectively. Another paper by Adam and Gordon¹⁰⁾ claims that Cl⁻ catalyzes the decomposition of OCl⁻ in the pH 9-10 range. Decomposition of HOCl at lower pH values is difficult to measure because any decomposition is overshadowed by the off-gassing of Cl₂ at these pHs.

Also of importance in EO water generation is the concept of conversion efficiency. Conversion efficiency, or the percentage of salt that can be converted into HOCl, is an important concern in EO water generators. Conversion efficiency is defined as the following:

$$\% \text{ conversion efficiency} = \frac{[\text{free chlorine}]}{[\text{initial salt}]} \times 100 \quad (7)$$

Conversion efficiency is important for a number of reasons. Obviously, greater conversion efficiency leads to a higher concentration of free chlorine in EO water while using a lower concentration of electrolyte in the

feed solution. Another important concern is corrosion. Cl⁻ is a significant catalyst of corrosion¹¹⁾. Therefore, lowering the concentration of Cl⁻ in EO water through use of generation technologies with greater conversion efficiency is one possible strategy to limit corrosion of EO water.

EO water generators

In theory, an EO water generator is a type of electrochemical cell that is used for the separation and oxidation state change of Cl⁻ and its counter ion. A generalized sketch of an electrolytic cell is shown in Figure 2 below:

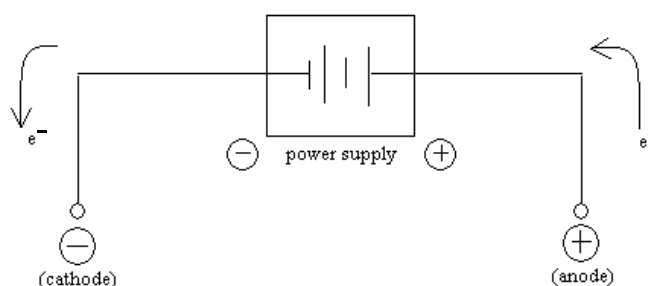


Fig. 2. Typical electrolytic cell
adapted from Bard and Faulkner¹²⁾

An electrolytic cell requires two electrodes and a power supply. The polarity of electron flow from the power source in Figure 2 indicates that the electrode on the left is a cathode, and the electrode on the right is an anode. The cathode and anode (which are negatively and positively charged in the figure, respectively) are best described by the types of redox reactions that happen around them. Reduction reactions happen at the cathode, and oxidation reactions happen at the anode. Both the power supply and electrodes will be covered in greater detail later in this review.

As mentioned previously, an EO water generator functions as an electrolytic cell. Due to the variation in EO water generator design, there is a great deal of difference in the operating parameters normally used by a generator. As such, the most essential parameters are the chemical requirements need for the desired reactions to occur. The functioning of the cell will depend largely on conditions such as amount and direction of the

electrical current and electrolyte concentration¹³).

In the operation of an EO water generator, a power source provides the electron flow that allows an electrical potential to develop in the cell. The size and direction of the potential will determine the nature of the reactions that happen at the electrodes. A relationship between potential and current is usually best described by a current-potential curve. A current-potential curve shows the potential needed to drive a reaction at a certain rate, which is known as the overpotential. In EO water generators, a potential of 2 V or greater is sufficient to cause the oxidation of chloride at the anode because the potential (vs. standard hydrogen electrode) of equation (3) above is 1.36¹²). Cell potentials in an EO water generator are set dependent on the electrolyte concentration, for the purpose of avoiding arcing¹³).

Several studies have confirmed that the amount of chloride present in the feed solution of an EO water generator will relate to the amount of free chlorine produced by the generator^{1,14}). The consensus is that an increase in chloride concentration in solution will lead to an increase in free chlorine concentration. However, there are other factors, such as hydraulic regime and solution residence time, that could have an impact on the value of Cl⁻ concentration as a variable for free chlorine formation.

Electrodes in EO water generation

Since electrodes are the sites where significant reduction of Cl⁻ to Cl₂ takes place, the electrodes are arguably the most important factors in EO water generators, as well as electrolytic cells in general. Electrolytic cells in general have 2 electrodes made from metal, typically titanium and stainless steel for the anode and cathode, respectively^{15,16}) or semiconductors. In addition to a metal core construction, electrodes are often coated with oxides¹⁶). Oxides made from iridium and ruthenium are the most commonly used, although studies have been undertaken with mixed oxide coatings, such as tin and iridium oxide¹⁷) as well as nickel and cobalt oxides¹⁸).

Also, precious metals such as platinum are sometimes added as part of the surface coating as well¹⁹). There are several reasons for coating electrodes. Coating an electrode helps to protect it from corrosion as well as increases the activity of the electrode.

Pure metal electrodes are not often used in applications involving chlorine solutions due to the risk of decreased output over time due to electrode surface corrosion. Oxide coatings reduce the oxidation of the metal electrode core by forming a passive barrier. The coatings also increase the interfacial area of the electrode, allowing for greater reaction rates.

Separatory membranes in EO water generation

Membranes are other factors which can affect the function of an EO water generator. The purpose of membranes in EO water generators is to divide the water to anode and cathode chambers and/or allow the selective movement of ions into the anode and cathode compartments of the electrolytic cell.

There are several different membrane types to consider: diaphragms, monopolar membranes and bipolar membranes. A typical diaphragm cell is pictured in Figure 3.

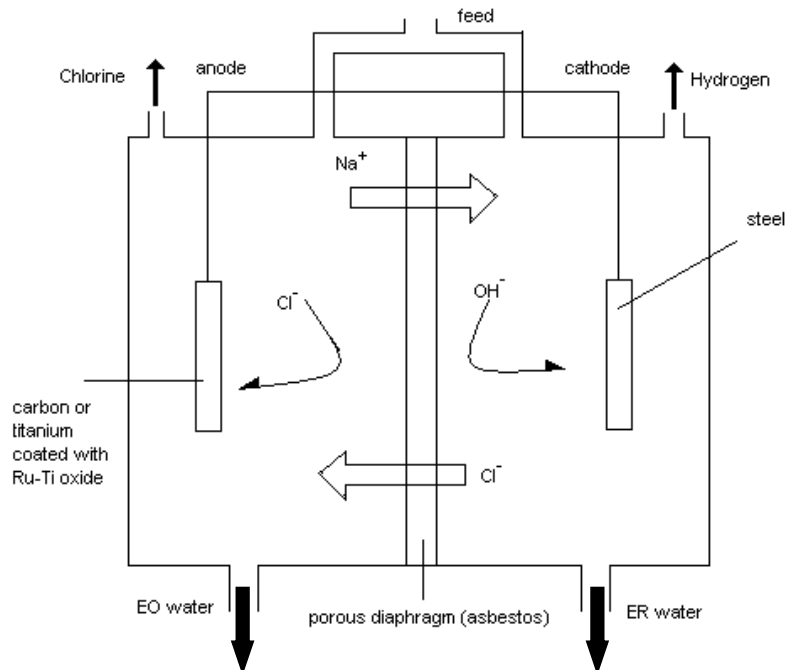


Fig. 3. Diaphragm Cell Model

Diaphragm cells make use of an asbestos “diaphragm” that resists the flow of hydroxide ions to the anode. Sodium ions are able to freely pass through the diaphragm. Additionally, some 7 chloride ions are able to pass through the diaphragm as well. In a sense, the diaphragm functions not as an impermeable wall (as the name diaphragm implies), but as a selectively-permeable membrane. Solvent is able to freely pass through the diaphragm but certain charged species are not. This method of separation of the cathode and anode compartments of the electrolytic cell is being replaced by monopolar and bipolar membranes, mainly due to environmental concerns associated with the asbestos diaphragm found in diaphragm cells.

Monopolar and bipolar membranes both have a standard design. The difference between a diaphragm cell and a membrane cell lies in the behavior of the partition (membrane) separating the anode and cathode chambers. Another difference lies in the composition of the cathode, which is usually nickel in membrane cells. Ion exchange membranes allow the flow of ions in a specific direction, dependent on the nature of the membrane, but not vice-versa. Generally, there are cation exchange membranes, which permit the flow of positive ions, and anion exchange membranes, which permit the flow of negative ions. Figure 4 is a model of an anion exchange membrane.

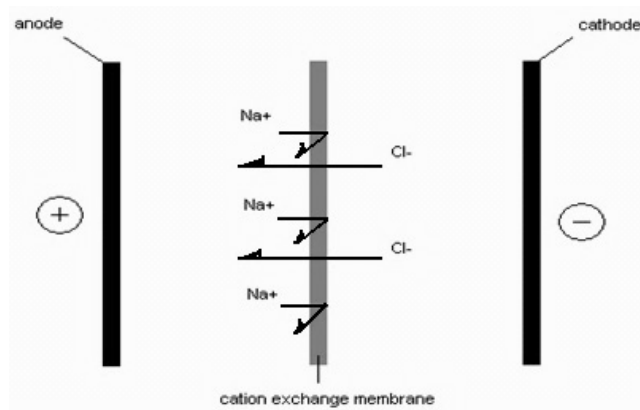


Fig. 4. Anion Exchange Membrane
adapted from Pabby *et al.* ²⁰⁾

Monopolar membranes are single-layered membranes that allow the selective transport of ions in the direction of charge. Specifically, anion exchange membranes only

allow the transport of negatively-charged cations while prohibiting the transport of positively-charged anions. In general, exchange membranes must have the following properties in order to be effective in EO water generation ²¹⁾:

- 1) A membrane must have the physical and chemical ability to withstand NaOH and Cl₂.
- 2) A membrane must have low electrical resistance.
- 3) A membrane must allow transport only Cl⁻ from the catholyte to the anolyte.
- 4) A membrane must operate at high current density.
- 5) A membrane must be immune to impurities (i.e. heavy metals) in the solution.

In contrast to the single layer design of monopolar membranes, dipolar membranes employ two different membranes with a hydrophilic layer sandwiched between them. An example of a dipolar membrane is shown in Figure 5.

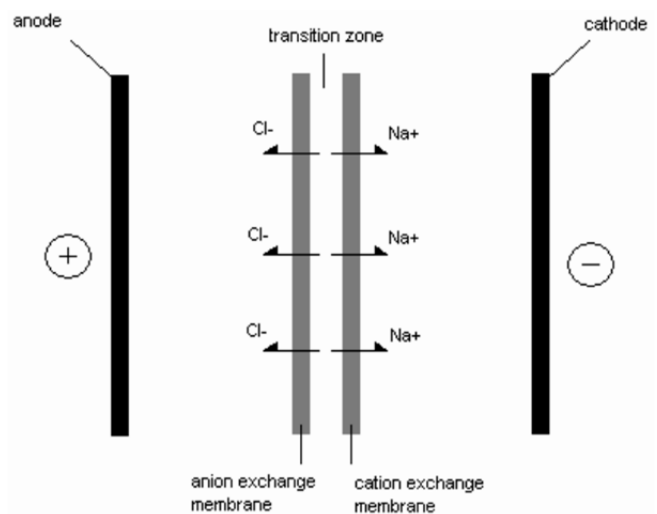


Fig. 5. Dipolar membrane
adapted from Pabby *et al.* ²⁰⁾

Figure 5 depicts a dipolar membrane that consists of a cation and anion selective membrane. Generally, ions in the transition region between the two membranes travel through the membranes in the direction of their charges ²²⁾. A special type of EO water generator with three chamber cells has electrolyte flowing through the middle chamber between the cation and anion membranes. Very pure EO water can be produced at the anode chamber. The membranes separate Na⁺ and Cl⁻ in the direction of current flow towards the cathode and anode, respectively.

This design is considered economical because of low power consumption, the ability to operate at high current densities; high acid and base concentrations can be produced, a high current efficiency and low maintenance costs⁵⁴⁾.

Generator parts in EO water generation

The power source of an EO water generator is one of the most basic parts of the generator that is not subject to modification. The power source provides an external voltage that is greater than the open circuit potential of the cell. In practice, a 120V power supply is commonly used. Some models of generators with adjustable voltage can range from 0-18V²³⁾.

The body of an EO water cell must be constructed with several considerations. First, the body must be water-tight to prevent the leakage of electrolyte solution onto open circuitry. Because of the corrosive nature of the solutions being used and produced, EO water generator parts are often made of plastics such as PVC.

In addition to concerns about the solutions being handled by the EO water generator, movement of different fluids through the generator is also important. The body must be constructed to allow the efficient import of electrolyte solution and the efficient export of EO water, ER water (if there is a separation between the anode and cathode), and gases such as oxygen and hydrogen. The accumulation of these gases in the generator could lead to an explosion hazard.

Factors affecting EO water generation

There are many factors both internal and external to an EO water generator that affect performance of the cell. One of the most important sets of factors are those relating to the electrodes. Electrode material, surface area, electrode geometry and surface condition must all be considered when addressing the contribution of the electrodes to an EO water generator's performance.

Electrode material has been the focus of several studies in EO water generation, such as the development of metal oxide coated metal^{16,24)}, mixed metal oxides coating metal^{18,25)} and doped carbon-based electrodes^{26,27)}. Electrode material was found to influence material yield (referred to as conversion efficiency), which is the fraction of the starting material converted into the

desired product¹⁵⁾. As mentioned previously, electrodes involved in chlorine production by salt electrolysis are mostly titanium coated with oxides from the platinum group. Ruthenium oxide, the most common coating, is often used with oxides of titanium, tin and iridium²⁸⁻³⁰⁾. For chlorine production involving hydrolysis of hydrochloric acid (HCl), carbon anodes are preferred. Electrode material will also influence other aspects of the process, such as overpotential, selectivity, lifetime as well as behavior under nonoptimal conditions¹⁵⁾.

The surface area and geometry of an electrode directly influence the function of EO water generators in several ways. First, the geometry of an electrode can influence energy consumption in the electrolytic cell. Both electrolysis and the movement of solution through the cell represent most of the energy consumption in an electrolytic cell¹⁵⁾. The energy cost of pumping solution can be minimized by the electrode having an open, porous construction. This type of electrode construction imparts less turbulence to solution flow. In addition to energy consumption, electrode geometry can influence reaction rate. A porous electrode has a higher mass transfer coefficient, allowing for a greater rate of reaction¹⁵⁾. Of particular note is that both desirable and undesirable reactions can have their rates influenced by electrode geometry. For example, cylindrical and coaxial configuration of electrodes are claimed to have a higher salt conversion rate than parallel plates. Also, coaxial cells use a ceramic membrane, which has the disadvantage of being fragile during transportation, but with a longer life span in use, compared with "plastic" membranes or diaphragms.

Surface condition, in this case, refers to corrosion, scaling or some other type of fouling of the electrode surface. These surface conditions of an electrode can be negatively affected by the presence of impurities in solution.

Internal factors affecting EO water generation

Mass transfer factors refer to the movement of molecules in bulk solution to the electrode surface region. Figure 6 below illustrates the concepts of the electrode surface region and the bulk solution:

The greater the rate of mass transfer, the more efficient the electrolytic process is. There are several

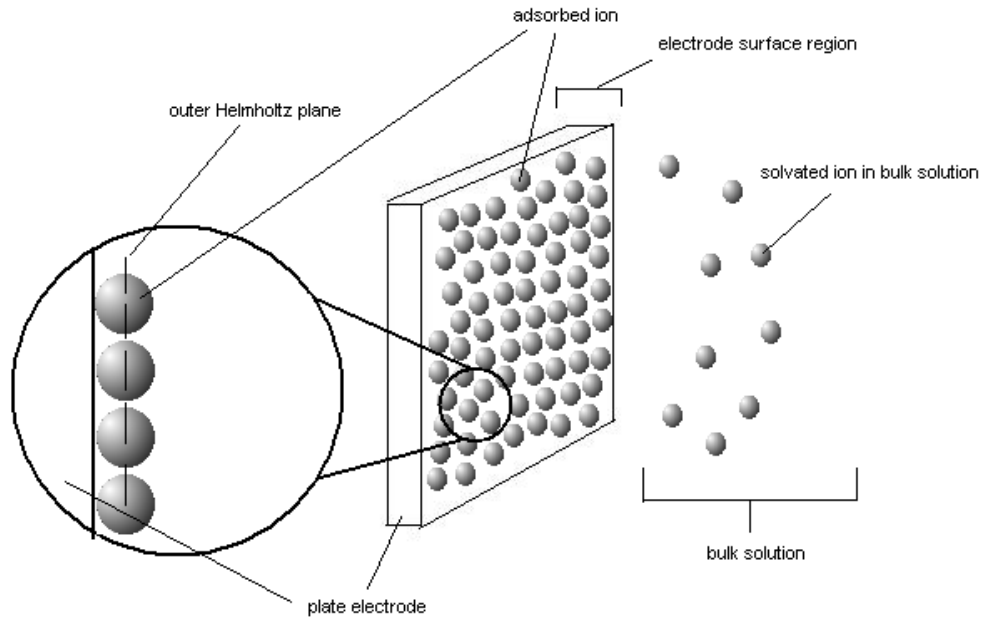


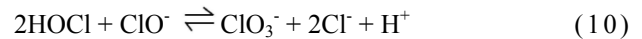
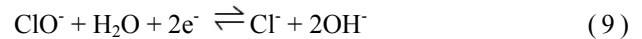
Fig. 6. Electrode surface region and bulk solution adapted from Bard and Faulkner¹²⁾

factors of mass transfer to be considered: mode of transfer, surface concentrations and adsorption.

Mode of transfer refers to the method by which solvated ions move from the bulk solution phase to the electrode surface region. Diffusion and convection are two examples of how transfer of solvated ions could occur. The mode of transfer applicable to particular electrolytic generator is usually dependent on factors relating to construction of the generator. Surface concentration refers to the density of solvated ions in the electrode surface region, and adsorption is defined as the method and rate which solvated ions adhere to the electrode surface. Both surface concentration and adsorption are influenced by electrode-specific factors (as discussed previously in this review) as well as factors relating to the solution itself.

Solution variables, such as bulk concentration of electroactive species, concentrations of other species as well as the nature of the solvent, all influence an EO water generator's function¹²⁾. The concentration of electroactive species (in this case, the concentrations of chloride ion and its oxidized electrolysis product, Cl_2) will influence the rate of electrolysis based on simple equilibrium mechanics. Low concentrations of chloride ion will cause a decreased production of Cl_2 (which is subsequently converted to HOCl). Likewise,

increasing the concentration of chloride ion will increase production of HOCl under many circumstances^{13,14)}. Other factors worthy of consideration are so-called "loss" reactions in electrolytic generators. Depending on the generator design, the following reactions could occur to a greater or lesser degree³¹⁾:



Reaction (8) takes place at the anode. OCl^- is oxidized along with water to produce chlorate (ClO_3^-) ions. At the cathode, ClO^- is reduced to Cl^- , as shown in (9). Reactions (10) and (11) both take place in solution. Overall, these reactions are said to be more prevalent when solutions from the cathode and anode are allowed to mix, as is the case for some EO water generation technologies.

Electrical factors, such as potential, current and quantity of electricity, also affect the rate of electrolysis¹²⁾. As mentioned previously, electrical potential is supplied by a 120V power supply in many cases. Work by Ezeike and Hung¹³⁾ concluded that voltage was an important contributor in the production of free chlorine. Generally, increases in voltage led to corresponding increases in free chlorine.

External factors affecting EO water generation

In addition to factors within the generator itself, variables external to the generator, such as temperature, pressure and time, can also influence the efficiency of the electrolysis process. The role of temperature in EO water generators has been explored previously^{1,14}. It was determined that temperature was significant in the determination of the magnitude of DC current and reaction rates. However, when compared with other variables such as salt concentration, the role of temperature was determined as not significant. For this reason, temperature is not regarded as an important factor in generator function¹.

In addition to temperature, pressure has been determined to play a role in function of a EO water generator^{32,33}. The role of fluid pressure in EO water generators is on gas solubility and concentration of Cl₂ in solution. In particular, increases in pressure lead to greater solubility of Cl₂ in solution. Decreases in the solubility of chlorine gas from a sample of EO water lead to decreases the level of free chlorine in the solution³⁴. The effect of pressure on Cl₂ concentration of EO water is only positive to a point, however. It is expected that eventually the Cl₂ concentration will provide a concentration barrier to the production of more Cl₂.

The discussion of time as a variable is limited to residence time of feed solution. It is expected that residence time of feed solution will be directly proportional to the concentration of free chlorine produced through electrolysis.

Common types of EO water generators

There are a wide variety of EO water generators available today. In Table 1 below, several EO water

generation technologies are compared by type of feed solution used, membrane type, the ability for a user to control pH and/or current, and the need for dilution before use.

Differences in feed solution among common generator types

Brine solutions are the most common types of feed solutions used in EO water generation. The chlor-alkali process in industry utilizes an estimated 90 million tons of salt per year³⁵, and the manufacture of chlorine is the largest single use of salt. Of the salts that can be used in EO water production, NaCl is the most commonly-used salt³⁶⁻³⁸. Other salts, such as KCl can also be used, but NaCl is more readily available and more economical. Since both the salts are readily soluble in water (both over 30g/100g of water at room temperature) and the potentials required for Cl⁻ oxidation at the anode are the same for both salts (-1.36 V), there is essentially no electrochemical difference between the two. EO water generators that use brine feed solutions are therefore the most common types of generators available, and the function of these types of generators is the most studied.

In contrast to salt, some EO water generators use HCl as a source of Cl⁻ ions. A few EO water generators are commercially available, especially for producing near neutral pH EO water. Outside of EO water generation, studies have been conducted to convert gaseous HCl waste into chlorine in order to address environmental concerns³⁹. One large difference that exists between NaCl and HCl is solubility. At room temperature, the solubility of NaCl is about 38 g / 100 g of water. In contrast, the solubility of HCl is approximately 70 g /100 g of water at room temperature. Theoretically, the higher solubility of HCl can lead to more Cl⁻ ions in solution for

Table 1. Comparison of Common EO water generation technologies

Generator	System 1	System 2	System 3	System 4	System 5
Feed solution	NaCl	NaCl	HCl	NaCl	NaCl
Membrane arrangement	single non-selective	single non-selective	none	single ion selective	none
pH control	yes	no	no	yes	no
Current control	yes	yes	no	no	no
Need for dilution	no	no	no	yes	no

*All systems are available in Dr. Hung's lab at the University of Georgia

electrolysis. Also, EO and ER water generated using HCl lacks Na^+ ions. This is beneficial for operation that caustic soda (NaOH) is not used. NaOH may also contribute to the production of oxygen radicals, like OH^\cdot and O^\cdot , which represent a more rapid path to corrosion than Cl^\cdot .

Differences in pH control among common generator types

In cases where pH control is needed, one method of pH control involves the restriction of ER water exit from the generator. Some generators are constructed in a way such that the back pressure created from doing this allows ER water to mix with EO water inside the cell. This is outlined in Figure 7 below:

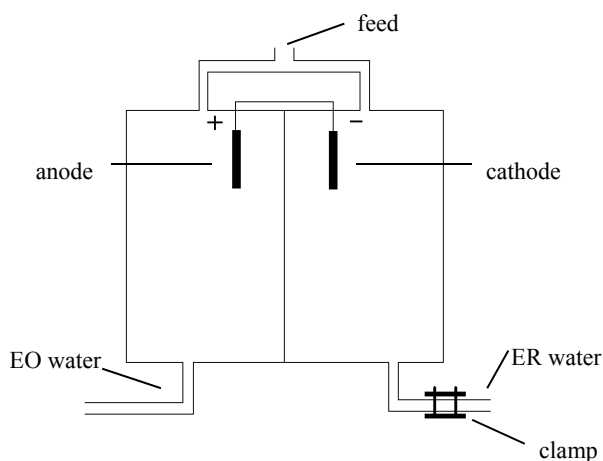


Fig. 7. pH control by back pressure

In Figure 7, feed solution enters the generator, and the electrochemical reactions occur in the same way as other EO water generators. The difference is that ER water flow is restricted as it exits the machine (in the case of Figure 7, by a clamp). This causes a buildup of pressure which forces some ER water into the anode chamber to mix with EO water. The near neutral pH EO water exits the machine from the EO water outlet. Essentially, the pH of the EO water can be adjusted by controlling the back pressure at the ER side.

Another method of pH control involves a recycling mechanism that allows alkaline water to be mixed with EO water, as illustrated by Figure 8.

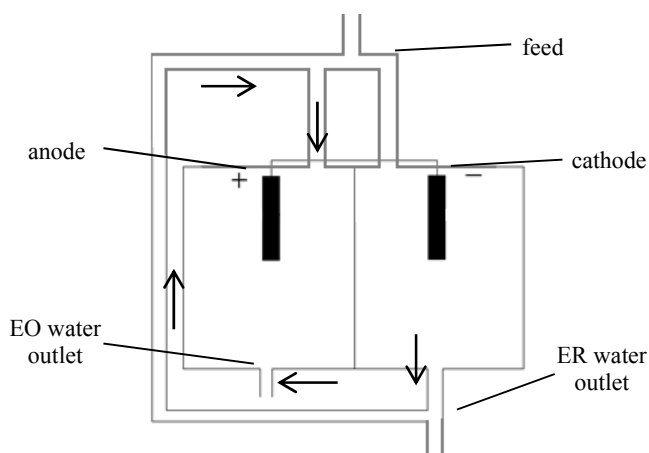


Fig. 8. pH control by alkaline water recycling

The arrows in Figure 8 represent the flow of alkaline water from the cathode to the anode, which results in an increase in sodium and hydroxide ions to produce an EO water solution of a higher pH.

Generators that produce acidic EO water have a division between the anode and cathode regions of the cell. This is done in order to prevent the anolyte from mixing with the catholyte. Another way to generate near neutral EO water is to not have a division between the anode and cathode⁴²⁾. This type of EO water has a pH typically between 5 and 7 and a lower ORP (~850 mV at pH 5)^{40,41)}. Table 2 summarizes the properties of acidic EO water and near neutral EO water.

Table 2. Comparison of acidic EO water and near neutral EO water properties

	Acidic EO	Near Neutral EO
<i>General chemical properties</i>		
pH	2.3-2.7 ^{3,59)}	5.0-6.5 ^{42,43)}
ORP	> 1000 mV ³⁾	800-200 mV ^{40,41,43)}
Primary chlorine species	HOCl , Cl_2 ¹⁰⁾	HOCl , OCl^- ^{8,58)}

The properties of acidic and near neutral EO water contribute to their stability and antimicrobial activity. In terms of stability, near neutral EO water is much more stable due to no loss of Cl_2 through evaporation and the relatively slow rate of ClO^- decomposition than acidic EO water^{43,44,45)}, which is more prevalent at lower pH values^{44,45)}. On the antimicrobial property, near neutral

EO water has a high percentage of chlorine in the form of hypochlorous acid and can compensate for its low ORP values.

Differences in current control and membrane technology among common generator types

Some EO water generation technologies allow the user to control the magnitude of the current through the electrolytic cell. As explained previously, increases in electrical current in an EO water generator result in increased concentrations of free chlorine. Besides this, current control can also allow control the rate of undesired reactions⁴⁶⁾. Current control allows for the prediction of energy consumption in a specific process⁴⁷⁾ as well as the efficiency of the process⁴⁸⁾. There are a few options available for current control. One such option is the use of amplifier instruments to regulate changes in potential or current⁴⁹⁾.

Membrane technology is not just limited to the specificity of the membrane. Often, the number of membranes and their arrangement can influence the efficiency of an EO water generator. Semipermeable, or selectively permeable, ion exchange membranes have already been introduced in this review. Cationic membranes, in particular, have been studied in some detail either alone^{50,51)} or in comparison to other types of membranes, such as diaphragms⁵²⁾. In the chlor-alkali industry, diaphragm cells are being phased out in favor of ion exchange membranes. Ion exchange membranes carry an advantage over diaphragms because the membranes have less of an environmental impact in terms of construction materials used in membrane production as well as power consumption. There are two types of ion exchange membrane configurations to consider: single and bipolar.

Single ion exchange membranes, as discussed earlier, allow a specific charge of ion to pass through while excluding counter charged ions. The membrane is used to physically separate the cathode and anode in an electrolytic cell. In the chlor-alkali industry, cation exchange membranes are most often used⁵³⁾. Cationic membranes are constructed of perfluorinated polymers (Nafion[®] polymers). The original Nafion[®] polymers

utilized sulfonic groups, however problems at high NaOH concentrations led to modifications⁵³⁾. Eventually, the single cation exchange membranes evolved into composite membranes. Composite membranes have a thin layer of carboxylate polymer on the cathode side of the membrane. The layer prevented the back migration of hydroxide (OH⁻) ion, and it was still sufficiently thin to keep membrane resistance low⁵³⁾.

Bipolar membranes (Figure 9) are cation and anion exchange membranes joined closely together. In the chlor-alkali industry, bipolar membranes are manufactured to be immersed in an electrolyte flow that runs perpendicular to the membranes below.

The design in Figure 9 enables single units of bipolar membranes to be used modularly as components in a rack. This design saves space and allows the individual units to be connected electrically in a series. Feed pipes carry brine to a distributor (not pictured) in a direction perpendicular to plane of view.

Differences in solution flow among common generator types

The flow of feed solution and product solution in an EO water generator is another factor worthy of consideration. For the chlorine manufacture industry, there is a compelling need to increase variables, such as mass transfer, that lead to higher product yields⁵⁵⁾. Previous work by Hsu¹⁾ indicated that increases in water flow rate increased electrolysis current. Other work by Hsu¹⁴⁾ as well as Ezeike and Hung¹³⁾ indicated that

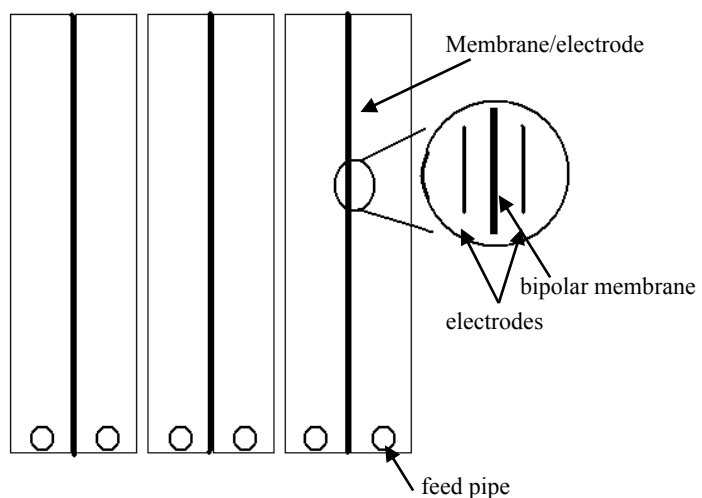


Fig. 9. Bipolar membrane unit configuration adapted from Schniders⁵⁷⁾

increases in water flow rate decreased the level of free chlorine in EO water. Both groups concluded that lower residence time of electrolyte within the cell led to a decreased level of free chlorine. However, generator design changes to increase residence time must not reduce the production rate/capacity. Increased residence time can be achieved through modification of speed that electrolyte passes through the cell or configuring the flow pattern in the cell to allow for multiple passes. Another way to modify residence time is to induce turbulence. Subbaiah and coworkers⁵⁶ reported that increasing turbulence enhances the mass transfer coefficient at the membrane surface, leading to higher yields in product.

Conclusions

There is a wide variety of EO water generation technologies commercially available. Due to differences in construction and operation, the exact definition and quality of EO water can be significantly different. Understanding EO water generators, in particular their design, components and factors effecting EO water generator performance can lead to the research and manufacture of safer and more effective EO water generators.

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