How Salt Generators Work

The Chlorine Generation Process:

Most of the packaged chlorine available today is manufactured by the salt process. There are three types of electrolytic cells: diaphragm, mercury and membrane. There are other methods of production, which are designed to fit the raw material containing the chlorine ion. These methods include the electrolysis of hydrochloric acid, the salt process, and the HCl oxidation process.

Electrochemical Cell

The electrochemical cell is composed of an anode, a cathode, and a separator which isolates the liquids contained in the anode chamber and the cathode chamber. The function of the separator is to isolate the two chambers while allowing the migration of selected ions from the anode chamber to the cathode chamber. Brine composed of sodium chloride and water is introduced into the anode chamber where oxidation of the sodium chloride takes place. Chlorine gas is released at the anode. The sodium ions are attracted to the negatively charged cathode and transported through the separator. Ideally, all of the chloride would be contained on the anode side of the cell.

Water is reduced at the cathode and hydrogen gas is evolved. The remaining hydroxide ion combines with the sodium ion to form sodium hydroxide solution (caustic), which exits the cathode chamber. Ideally, all of the hydroxide ions would be contained on the cathode side of the cell.

Membrane Cell

In the membrane process, the anolyte (the solution in the anode chamber) and the catholyte (the solution in the cathode chamber) are separated by a cation exchange membrane that selectively transmits sodium ions but suppresses the migration of hydroxyl ions from the catholyte to the anolyte. This produces a catholyte effluent with a strong caustic soda solution with a very low sodium chloride content. The advantage of the membrane process are its energy efficiency and its ability to produce, without any harmful effect on the environment, a strong, high-quality solution of caustic soda (NaOH).

The overall chemical reaction is:

$$NaCl + H_2O + \text{electric current} \rightarrow NaOH + 1/2\ Cl_2 + 1/2\ H_2$$

The two reactions that make up this overall reaction are:

The principal anode reaction:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Chlorine formed at the anode saturates the anolyte and an equilibrium is established as follows:

$$Cl_2 + (OH)^- \rightarrow Cl^- + HOCl$$
$$HOCl \leftrightarrow H^+ + OCl^-$$

This shows that the chlorine is formed and then makes the chloride ion (Cl-), and the hypochlorous acid (HOCl), which further dissociates in equilibrium to hypochlorite ion (OCl-) and hydrogen ion (H+).

The principal cathode reaction is: $2H^+ + 2OH^- + 2e^- \rightarrow H_2 + 2OH^-$

The hydrogen ion (H+) present in the H_2O in the catholyte evolves at the cathode as hydrogen gas (H_2), leaving behind the hydroxyl or hydroxide ion (OH-) in the catholyte. Because chlorine has evolved at the anode, the sodium ion (Na+) is free to join the hydroxide ion (OH-) as it migrates from the anolyte chamber to the catholyte chamber. The porous diaphragm is used to inhibit the migration of the OH- ions from the cathode to the anode.

Ideally, we produce pure hydrogen gas, pure chlorine gas and pure sodium hydroxide in this process.

Mercury Cell

The mercury cell has two essential parts: (1) the elctrolyzer and (2) the amalgam decomposer. In the elctrolyzer, a salt solution is electrolyzed, making use of a special anode and a flowing mercury cathode. Chlorine gas is liberated at the anode, and sodium is deposited at the surface of the flowing mercury cathode, in which it dissolves to form a liquid amalgam. The amalgam flows to the decomposer where it is decomposed with water to form sodium hydroxide and hydrogen gas. The mercury is then recovered and reused.

In the 1970s, mercury cell operations in the U.S. were found to be discharging effluents containing mercury in excess of the safe limits established by EPA. Some installations were shut down. Those that were not shut down improved the process to the point where the effluent mercury level was below the maximum allowed. There are 91 mercury cell chlorine plants in the world producing more than 11,000 tons of chlorine per day.

The swimming pool industry had a few companies that used a brine solution with a membrane. I am not sure that any of them are in business today. The one I remember was from Unichlor which grew out of Pinch A Penney in Florida. These units, very effective, and I have still seen them around. Some operational, some not.

Most chlorine generators in the swimming pool industry today use what is called an in-line system. This is a device that contains many cells with pool water passing through it. Salt (sodium chloride) is added to the pool water to a level of 2000 to 6000 ppm depending on the manufacturer. Low voltage DC electricity is applied to the cells and the unit produces chlorine gas, hydrogen gas, sodium ions, hydroxide ions. However, there is no membrane or separator and the direct mixing of these products result in the formation of sodium hypochlorite instead of the evolution of elemental chlorine gas. The sodium hypochlorite quickly makes hypochlorous acid (HOCl – the killing form of chlorine) and hypochlorite ion (OCl-). The hydrogen gas releases into the atmosphere as it bubbles up into the pool water. Very little of the hydrogen is in the ionic form in the water. The hydroxide stays in the pool water and will slightly raise pH.

Many industry people and some chemists are of the opinion that in-line chlorine generators will not change the pH of the water. In theory this is true. The logic is that you start with a neutral salt (NaCl) split it into sodium and chlorine and put it all back into the water. However, the hydrogen gasses off which would have offset the hydroxide production if it stayed in the water. But since the hydrogen gas left the water the hydroxide will raise pH - once the TA is balanced the pH will also level off around 7.8.

The other questions seemed to be regarding caustic soda and why it is in sodium hypochlorite.

First, let me say that if you make sodium hypochlorite and do not use any caustic, your solution will have a shelf life of a couple of days. Second, let me explain how sodium hypochlorite is made.

Start with a solution of caustic soda (sodium hydroxide) and bubble chlorine gas through it. This makes sodium hypochlorite , sodium chloride, water and heat.

Here is the reaction:

$$2\ NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O + Heat$$

One the basis of molecular weight, 1 lb chlorine reacts with 1.128 lb caustic soda to produce 1.05 lb of sodium hypochlorite and 0.83 lb of sodium chloride. In practice, an excess of caustic soda is used as a stabilizer. A 10% sodium hypochlorite solution has about 10 grams per liter excess caustic soda. A 12% sodium hypochlorite solution has about 12 grams per liter excess caustic soda. A 15% sodium hypochlorite solution has about 15 grams per liter excess caustic soda.

My primary purposes for this lengthy explanation is to show you that the chlorine generator (salt generator, hypochlorite generator) is not exactly the same as the industrial versions and that they make pure, elemental chlorine gas that is then captured and stored under pressure in large steel cylinders. Pool chlorine generators make elemental chlorine gas too but, because it is made in the water, it instantly makes hypochlorous acid and hypochlorite ion. They do not make sodium hypochlorite.

Methods of Operation

There are normally two ways a salt generator works. One is by varying the amperage to the cell. Since cell life is generally based on how long the cell is in operation and not how much chlorine is produced, this is not always the best method.

The second way is to keep the amperage on its highest setting and vary the length of time it is on via a timer. The timer can be internal or external or both. For example, in a pool of 30,000 gallons; the filter may be running 24/7. The salt-water chlorine generator could be on a separate external timer to only operate from 9:00 pm to 9:00 am. The internal timer on the unit could be adjusted to fine tune the production of chlorine. NOTE: A salt-water chlorine generator should NEVER be on when there is no flow / pump is off.

Based upon calculations of one pound of chlorine per 10,000 gallons = 12 ppm; the unit being on 12 hours per day, the setting on the unit would need only be dialed in at about 25% production to achieve 1 ppm. In reality, I would start at 25% production the and adjust by observing the swim load, sun, heat, rain, animals etc.