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DISINFECTANTS FOR PUBLIC SWIMMING POOLS

CHLORINE GAS	
Formula:	Cl_2
Modular Weight:	70.94 g/mole
Density:	1.25 g/liter (4.75 g/gal)
Chemical Reaction:	$Cl^2 H^2O \longrightarrow$ HCl + HOCl

Chlorine is a poisonous, caustic, yellow-green gas. It is 2.5 times heavier than air, sinks and accumulates rapidly on the ground. Usually, chlorine gas comes liquefied under pressure in steel bottles for transportation. There are two potentially dangerous aspects of using chlorine gas, the level of toxicity (90 mg/m^3 (90 ppm) deadly concentration) and the storage of the bottles under 150 psi (10 bar). See Table 1 below.

Table 1: Chlorine concentrations in the air and symptoms in humans

Concentration ppm	Effect on Humans
0.05-1	Detectable Odor
1	No risk at longer exposures
4	Tolerable for a couple of minutes (unsuitable working conditions).
10	Bronchitis after 1 hour.
15	Immediate burning of the eyes.
30	Possible coughing-inflammation of the lungs after 1½ hours.
50	Inflammation of the lungs, death after 1½ hours.
500	Death after 5-10 minutes.
1000	Immediate death after a few breaths.

Chlorine gas is the most favorable disinfectant strictly from operating cost. In spite of the high investment costs for a chlorine gas regulation and control system, it is this system which seems to have the best life cycle cost.

However, because of the hazards and precautions which must be taken when using chlorine gas, this system is being phased out.

There are various other chemicals which are used as disinfectants in swimming pools. These chemicals are sodium hypochlorite NaOCl, calcium hypochlorite Ca (ClO_2), trichloro-isocyanurate Cl_3 $(NCO)_3$ and sodium dichloro-isocyanurate $NaCl_2(NCO)_3$. All these compounds create hypochlorous acid (HOCl) or free chlorine by reaction and water. The completion of this process depends on the disassociation and oxidation effects of water. A byproduct of the reaction, (HOCl) results as a compound which is significantly influenced by the pH-value of the water.

SODIUM HYPOCHLORITE

Sodium hypochlorite has the advantage over chlorine gas of being simpler and less dangerous to handle. It is necessary as usual to be careful when handling and requires the use of chemically resistant injection pumps and piping. These pumps must be adjustable by the quantity of fluid per pumping cycle and by variable cycle frequency and are called peristaltic pumps.

Typically sodium hypochlorite solutions with 150-170 g/liter (570-645 g/gal) active chlorine have a concentration of around 13% hypochlorous acid. The pH-value of the solution lies between 10 and 11.

Sodium Hypochlorite	
Formula:	NaOCl
Active Chlorine:	150-170 g/liter (570-645 g/gal)
Density:	1.25 g/liter (4.75 g/gal)
Chemical Reaction:	NaOC + $\longrightarrow$ H_2O NaOH + HClO
Chemical Decay:	3NaOCl $\longrightarrow$ $NaClO_3$ + NaCl
Active Chlorine Loss:	1 g/liter day (3.8 g/gal day)
Temperature Range:	15-20 C (59-68 F) at 150 g/liter

Sodium hypochlorite solutions are perishable. The decay and the concentration of the active chlorine is lost over time. With this decaying reaction no chlorine gas is produced and only sodium chloride and oxygen are produced. This decay will be accelerated by higher temperatures, direct radiation from the sun and from the presence of heavy metals. At room temperature active chlorine concentrations will maintain a calculated loss of about 1 g/liter per day (3.8 g/gal day). When ordering be careful that the storage time is short before using (frequently order small containers).

The decay is dependant on the concentration of the solution. Strongly concentrated solutions decay faster. If concentrated sodium hypochlorite is being delivered, then immediate dilution at the site should be considered.

CALCIUM HYPOCHLORITE (INORGANIC SOLID CHLORINE)

Calcium hypochlorite exists in granular form, either in powder or pressed tablets. Calcium hypochlorite has an active chlorine content from 65-72% and also contains 2% calcium hydroxide, 10-11% sodium chloride, 10-11% Calcium carbonate and 10-11% calcium chloride.

Calcium Hypochlorite	
Formula:	$Ca(ClO_2)$
Active Chlorine:	65-72%
Chemical Reaction:	$Ca(ClO_2)$ + 2 H_2O $Ca(OH)_2$

Calcium hypochlorite dissolves in water and develops a milky, cloudy solution. This turbidity is created in part through calcium hydroxide and calcium carbonate precipitation. A 1% calcium hypochlorite solution has a pH-value of 10-11. With medium to hard water calcium carbonate can come out of solution into the pool water. In addition to a milky or turbid pool water, which will be interpreted as dirty water to the pool guest, the increase in insolvent lime will cause resistance to water flow through the filter medium. It will cause the pressure drop across the filter to climb quicker and result in shorter time intervals between backwash cycles. Side stream filter stations can be used to remove the undissolved solids from the pool water. This will help in providing pool water with a better clarity.

CHLORINE-ISOCYANURIC ACID

The use of the following chemicals is based on isocyanuric acid stabilization of active chlorine in the pool water. The difference between the fast acting solution sodium dichloro-isocyanurate (with solubility in water of about 250 g/liter (950 g/gal and an active chlorine content of 60-63%) and the less soluble trichloro-isocyanurate (with a maximum solubility of 12 g/liter (45 g/gal) and an active chlorine content to 90%) should be recognized.

Sodium Dichloro-Isocyanurate

Formula:
$NaCl_2(NCO)_3$ / $NaCl_2(NCO_3)$ 2 H_2O

Active Chlorine:
60-63% / 56%

Chemical Reaction:
$NaCl_2(NCO)_3 + H_2O \longrightarrow 3\ H_2O +$
$C_3N_3O_3H_3$

Trichloro-Isocyanurate

Formula:
$Cl_2(NCO)_3$

Active Chlorine:
80-90%

Chemical Reaction:
$Cl_3(NCO)_3 + 3\ H_2O \longrightarrow 3\ H_2O +$
$C_3N_3O_3H_3$

The use of these compounds as disinfectants are being discussed throughout the world because the cyanuric acid acts as a stabilizer and extends the life of active chlorine in water. This is especially desirable for outdoor pools subject to direct UV radiation from the sun and in motion pools or pools with water attractions.

However, it must be pointed out that higher concentrations of isocyanuric acid in pool water do not offer better bactericidal effects. That is, measured and calculated examinations of isocyanuric acid in water have shown that there is a good relationship between the stabilization effect of isocyanuric acid and the content of free chlorine to maintain a sufficient germ mortality rate when used within the following parameters:

Free chlorine concentration between 0.6 and 1.2 mg/liter (0.6-1.2 ppm) with a maximum concentration of 40 mg/liter (ppm) of isocyanuric acid.

CHLORINE-ELECTROLYSIS PROCESS W/COOKING SALT

The chlorine-electrolysis process produces chlorine gas on site directly from sodium chloride (cooking salt). The process chlorine gas reacts with sodium hydroxide formed in water to form sodium hypochlorite. The resulting solution has a concentration of 2-5 g/liter active chlorine. About 20% of the process flow of the sodium chloride solution will be effectively reacted. To manufacture 1 kg (2.2 lb) chlorine gas about 3-4 kg (11-15 lb) of sodium chloride and 5-6 kWh of electricity are required.

If the high content of sodium chloride in the swimming pool water annoys or disturbs the guests or causes unfavorable effects on building materials, like corrosion of steel in filters or heat exchangers, then a membrane technology can be used for the separation of chlorine gas from the other products of the reactions as shown by the following reactions.

Reaction 1:
$2\ NaCl + 2\ H_2O \longrightarrow 2\ NaOH +$
$\uparrow H_2 + \uparrow Cl_2$

Reaction 2:
$2\ NaOH + Cl_2 \longrightarrow NaCl + H_2O$

The resulting chlorine gas from Reaction 1 will be directed into the swimming pool water and the hydrogen gas is vented off. The hydrogen gas is vented in accordance with NFPA regulations to limit the concentration of hydrogen in air to less than 1% by volume. The excess chlorine gas reacts with the sodium hydroxide in water in Reaction 2 and the resulting solution is pumped back to the salt solution holding tank.

It is recommended that a vapor detector alarm system calibrated for chlorine be provided. If the detector senses the presence of trace amounts of gas outside the system the generation process will be shut-down and an alarm will be sent to the building engineer.

CHLORINE-ELECTROLYSIS PROCESS WITH HCL

Another process which is frequently chosen is the chlorine-electrolysis process using hydrochloric acid (sometimes called muriatic acid when diluted). The electrolytic process is the same as for sodium chloride where electricity is used to generate the chlorine gas. To manufacture 1 kg (2.2 lb) of chlorine gas 3.3 kg (12.5 gal) 33% HC1 and 2-2.5 kWh of electricity are required.

Reaction 1:
$2\ HCl + H2O \longrightarrow \uparrow Cl_2 + \uparrow H_2 + H_2O$

In this process a 33% solution of hydrochloric acid in water is stored in an acid storage tank and is pumped to the electrolytic reactor. The dissociated hydrogen and chlorine ions are combined using electricity. The resulting chlorine gas is stripped off using a semipermeable membrane and the water flows through the reactor into a hydrogen gas separator. The hydrogen gas vents off and a small flow of water returns to the surge tank.

Both of these electrolytic processes are similar whereby distilled water for dilution of either cooking salt or hydrochloric acid is used to reduce the build-up of calcium carbonate (lime) on the electrode. The electrodes used in hydrochloric acid electrolytic reactors must be replace more often because of the aggressive nature of the acid solution.

FINAL REMARKS

Independent of the type of disinfectant used, it is important to realize that the pH-value of the swimming pool water influences the concentration of free chlorine in water. To optimize the disinfecting effect of chlorine the pH-value must be maintained between 7.2 and 7.4 and be regulated and monitored regularly. It is necessary to monitor the free chlorine, total chlorine, pH-value and oxidation/reduction potential frequently. This is best accomplished using modern automatic electronic regulation and registration equipment which regulates the water quality and provides a continuous record of the desired chemical parameters. This is the best way to provide continual optimal water quality to the pool guests and at the same time minimize chemical usage.

BIBLIOGRAPHY

* Beddow, B., 1995. Planning, Construction and Operation of Whirlpools, Leesburg, VA.

- Beddow, B., 1995. Ventilation in Natatoria, Leesburg, VA.

* Deutsches Institut für Normung (DIN 19643), 1993. Aufbereitung von Schwimmund Badebeckenwasser. Berlin, Germany.

- Eichelsdorfer, D. Jandik, J., Weil, L. Volume 5, 1981. Bildung und Vorkommen von organischen Halogenverbindung im Schwimmbeckenwasser. *Archiv des Badewesens.* Wiesbaden, Germany.

* Herschman, W., 1980. Aufbereitung von Schwimmbadwasser. *Krammer-Verlag.* Düsseldorf, Germany.

- Kannewischer, B. Volume 1, 1993. Badewasserdes infection mit Chlorgas und mögliche Alternativen. *Umwelttechnik*. Zürich, Switzerland.

- Kannewischer, B., 1988. Optimieruug der Wasseraufbereitung in öffentlichen Hallen – und Freibädern, *Umwelttechnik*. Aug Switzerland.

- Kannewischer, B., 1979. Badewasseraufbereitung für öffentliche Bäder. *BAG Brunner Verlag.* Zurich, Switzerland.

- Kurzmann, A., 1978. Schwimmbeckenwasser aufbereitung mit oder ohne Ozon. *Beratungsbüro und Laboratorium für Ozon - und Wasser - Technologie.* Walldorf, Germany.

- McGregor, R., Walenczak, W., Rogers, R., Magnetti, L. Volume 2, 1993. Case Study: Ozone-Based Water Treatment for High - Quality Air and Water in a Municipal Swimming Center. *Proceedings: Eleventh Ozone World Congress.* San Francisco, CA.

- Mood, E.W., 1981. Public Swimming Pools: Recommended Regulations for Design and Construction, Operation and Maintenance. *American Public Health Association.* Washington, D.C.

- Pacik, D. Volume 4, 1992. Trihalogenmethanein neues Problem? *Archiv des Badewesens*. Wiesbaden, Germany.

- Pitrak, P.J., Rennell, D.S. Second Edition, 1992. Basic Pool & Spa Technology. *National Spa and Pool Institute.* Alexandria, VA.

- Primarvesi, C.A., Althaus, M., 1980. Wert Bestimmung für das "Hydrozon-Kompaktverfahren" durchgeführt durch das Hygiene-Institute des Ruhrgebiets, Gelsenkirchen. *Hygiene-Institute*. Gelsenkirchen. Germany.

- Roeske, W., 1980. Schwimmbeckenwasser Anforderungen – Aufbereitung – Untersrchung; *Verlag otto Haase*, Lübeck, Germany.

- Saun, C., 1989. Planung von Schwimmbä dern, Bau und Betricb von privaten und öffentlichen Hallen – Sowie Freibäern einschlie Blich Whirlpools and Medizinische Bäder, *Krammer – Verlag*, Düsseldorf, Germany