Hypochlorite

Hypochlorites are salts of hypochlorous acid, usually supplied as sodium hypochlorite (NaOCl) solution or (less popularly) as solid calcium hypochlorite (Ca(OCl)2).

From: An Applied Guide to Water and Effluent Treatment Plant Design, 2018

Related terms:

Hydrogen Peroxide, Chloride, Sodium Hypochlorite, Disinfectant, Ion, Chlorine, pH Value

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Introduction to Food Irradiation and Medical Sterilization

Laurence McKeen, in The Effect of Sterilization on Plastics and Elastomers (Third Edition), 2012

1.3.3.2.1 Hypochlorites

Hypochlorites, the most widely used of the chlorine disinfectants, are available as liquid (household bleach, sodium hypochlorite) or solid (common pool chlorine, calcium hypochlorite). The hypochlorite ion, also known as chlorate (I) anion, is ClO₋. Household bleach is an aqueous solution of 5.25%–6.15% sodium hypochlorite.

Hypochlorites have a broad-spectrum of antimicrobial activity. They do not leave toxic residues, are unaffected by water hardness, are inexpensive and fast acting. They remove dried or fixed organisms and biofilms from surfaces and have a low incidence of serious toxicity.

One danger is the release of toxic chlorine gas when mixed with ammonia or acid (e.g. household cleaning agents). The microbicidal activity of chlorine is attributed largely to undissociated hypochlorous acid (HOCl). The dissociation of HOCl to the less microbicidal form (hypochlorite ion OCl–) depends on pH. The disinfecting efficacy of chlorine decreases with an increase in pH that parallels the conversion of undissociated HOCl to OCl–.

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Homogeneous Catalysis

JohnBurgess, Colin D.Hubbard, in Advances in Inorganic Chemistry, 2013

2.10 Hypochlorite

Hypochlorite and chlorine have long been used as disinfectants and bleaching agents in a wide variety of circumstances, at least since the eighteenth century (Eau de Javelle). An extensive review of their use in water treatment (154) includes discussion of a number of reactions and mechanisms of relevance to dye bleaching (Section 5). However, their aggressive character and the environmental consequences of their use have also long encouraged the search for benign but effective alternatives. This has to a considerable extent driven research and development into the bleaching and detergent properties of peroxoacids and their anions. This is particularly true for perborates, in relation to such materials as laundry bleaches, domestic cleansers, and denture-cleaning formulations. To give just one example of the fact that perborate can be as effective as hypochlorite, we cite the recent report of their effectiveness in stain removal from acrylic resin dentures. Both were good for bleaching turmeric stains, both were rather less effective in removing coffee stains (72). The powerful oxidizing powers of hypochlorite and chlorine have led to their use for detoxifying chemical warfare agents such as mustard gas, (CICH₂CH₂)₂S, the nerve gas VX, (EtO)MeP(O)SCH2CH2NiPr2, Sarin, (iPrO)MeP(O)F, and related agents of the R3PO type (78).

Comparisons between the behavior of peroxoanions and of hypochlorite have also been of value in relation to the determination of bleaching mechanisms of organic dyes, as will emerge in Section 5.

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Group 17 (H, F, Cl, Br, I) Alkaline Earth Compounds

R.C. Ropp, in Encyclopedia of the Alkaline Earth Compounds, 2013

Magnesium Hypochlorite

Magnesium hypochlorite has the chemical formula of $Mg(OCl)_2$ and the molecular weight of 127.286 g/mol. Its assigned CAS number is 10233-03-1. It can be prepared by reaction of hypochlorous acid upon magnesium carbonate in water. However, the product is not stable in water and decomposes to form basic magnesium hypochlorite, $Mg(OCl)_2 \cdot 2Mg(OH)_2$, which is useful in bleaching and sanitizing applications. The structure of this compound remains unknown.

A better process for the production of pure dibasic magnesium hypochlorite is said to comprise the reaction of a solid magnesium salt and a solid hypochlorite where one of the solid reactants is in the hydrate form. The process produces dibasic magnesium hypochlorite with excellent recovery of chlorine values and with reduced requirements for the disposal of solutions containing available chlorine. In this case, the reactants are magnesium chloride hexahydrate with calcium hypochlorite and its hydrates as preferred solid hypochlorite reactants:

 $MgCl_2 \cdot 6H_2O + Ca(ClO)_2 \Box Mg(ClO)_2 + CaCl_2 \cdot 6H_2O$

wherein the solid components are reacted together by fusion at an elevated temperature. In general, the product is a mixture of compounds that is similar to the compound known as "bleaching powder"

Basic magnesium hypochlorite, $Mg(OCI)_2 \cdot 2Mg(OH)_2$, is a solid compound having an available chlorine content in the range of from about 50 to 60%. Textiles are bleached by immersing them in an aqueous solution of this salt. Bleaching takes place at any suitable temperature such as those in the range of about 10 - 100 °C, but preferably from about 30 to 80 °C. Textiles are held in contact with the aqueous solution of dibasic magnesium hypochlorite for a period of time sufficient to provide the materials with the desired degree of bleaching.

This salt is available commercially but has not found widespread usage since the calcium hypochlorite salt is cheaper and just as effective in these applications.

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Pre-treatment and preparation of textile materials prior to dyeing

A.K. Roy Choudhury, in Handbook of Textile and Industrial Dyeing, 2011

3.17.3 Hypochlorite bleaching of cotton

Hypochlorite bleaching is a low-cost process using simple chemicals. The process was once very popular, but is now being phased out because of the following disadvantages:

- 1. It is not eco-friendly since it releases effluent of high AOX value. It is therefore banned in many countries.
- 2. There is a risk of fabric damage if the pH is low.
- 3. The process is slow and is to be carried at low temperature. Hence, it is difficult to carry out as a rapid continuous operation.
- 4. There is a chance of yellowing of bleached fabric on storage.
- 5. It releases relatively high concentrations of salt in the effluent process water, which is objectionable from an ecological point of view.

Two chemical compounds are utilised in hypochlorite bleaching – bleaching powder and sodium hypochlorite. The bleaching mechanism with chlorine-containing compounds is based on saturation or rupture of double bonds. The first mechanism is hydroxychlorination to a chlorohydrin (Equation [3.3]), the second mechanism is chlorination to form 1,2 dihalide (Equation [3.4]) and a third mechanism involves oxidation by electrophilic substitution, which destroys carboxyl chromophores (Mock, 1985).

[3.3]

[3.4]

The hypochlorite bleaching process has declined considerably due to ecological problems. When bleaching small quantities in long liquor (material:liquor [M:L] ratio about 1:5), a solution containing 1.5–2.75 g/L of available chlorine may be used for a treatment time of 2 h. However, for a circulating system as above, the M:L ratio may be as low as 1:1 and the available chlorine falls rapidly in the early stages. A liquor containing 8–10 g/L of available chlorine may be used in such cases and the circulation may be continued for 6–10 h.

After bleaching with bleaching powder, some calcium carbonate, formed by reaction of calcium hydroxide with atmospheric carbon dioxide, is deposited on the material. Hence an after-wash with mineral acid, termed 'souring', is essential to remove such deposits. The same treatment is also used for removal of residual chlorine after sodium hypochlorite bleaching. The material is finally washed to remove traces of acid, which may otherwise form hydrocellulose. The material is to be thoroughly washed before acid treatment. Generally, a treatment time of 30 min to 1 h with 1% sulphuric acid at room temperature is sufficient.

A better method for removal of residual chlorine, particularly after bleaching with sodium hypochlorite, is to treat the material at 40°C for 15 min in liquor containing 2–2.5% (o.w.m.) a reducing agent like sodium sulphite, bisulphite, hydrosulphite or thiosulphate.

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Dish and Household Cleaning

Gregory Szewczyk, Karen Wisniewski, in Handbook for Cleaning/Decontamination of Surfaces, 2007

2.1.1.4. General surface disinfectant cleaning

Hypochlorite bleach is the first example of a disinfectant compound commonly used in household cleaning. Counting household bleach and bleach-containing cleaners globally, "chlorine" bleach is probably the highest tonnage household disinfectant. Because bathroom surfaces like ceramics, methacrylate, or cement are not sensitive to bleach, it is commonly used in the bathroom. Household disinfecting is not the only use for hypochlorite bleach which reaches high tonnages (12 million tons in North America [42]) because much of it is sold as household bleach, a 5% solution of hypochlorite stabilized with alkalinity, intended as a general use product. Bleach is used as well in municipal water treatment and swimming pool maintenance. However, whitening and stain removal in laundry are still the biggest volume for household uses.

Peroxides are not often cited as disinfecting compounds. This may be due to their relative instability and short residence time on the surface. However, peroxyacids have been cited as antimicrobials, and not only as bathroom cleaners [43–45].

Quaternary ammonium surfactants or "quats" (QACs, see Figure B.2.I.1.) are widely used in consumer products especially as surface modifiers. They have been used as fabric softeners, antistatic agents, hair conditioners, phase transfer agents, and modifiers of drilling muds. Quats have many advantages including low odor (unlike phenols, chlorine bleaches, or pine oils), low color, high stability, and relatively low toxicity (unlike phenols or heavy metals) [46]. Quats used as disinfectants have structural elements particular to their antimicrobial efficacy; the most popular ones derived from benzyl chloride. Quats are widely used as disinfecting agents in bathroom cleaners, usually at levels not exceeding 0.5%, although they can range from 0.1 to 3%. The usage level depends on the pH of the cleaner. Quats are less effective as disinfectants at neutral pH and are effective disinfecting compounds usually between pH 2–4 or 8–10 [47,48]. Lower concentrations are used in cleaners in these acid and alkaline ranges, with higher concentrations found in cleaners formulated closer to neutral pH. In bathroom cleaning, low pH is desirable for soap scum removal. Higher pH "built" formulas are also made for bathroom cleaning, despite this being less effective for soap scum removal, but these formulas inevitably make disinfectant claims based on quats.



a. Alkyl dimethyl benzyl quaternary ammonium chloride



b. Dialkyl dimethyl quaternary ammonium chloride





Figure B.2.I.1. Structure of germicidal quats. Chloride is the usual counterion, although bromide is also used. Cyclic quats are less popular than the noncyclics

The drawback with quats is that they are cationic surfactants. If added together in 1:1 molar ratios, a quat and an anionic surfactant (such as sodium linear alkylbenzene sulfonate ("LAS") or soap), the two form insoluble complexes. Ratios differing from 1:1 may form less precipitates (due to solubilization of the complex by the excess surfactant) but the disinfecting activity of the quat is usually quenched by this interaction. Quat disinfectant formulation is therefore restricted to nonionic or zwitterionic (betaine) surfactants as the cleaning ingredients. Since anionic surfactants tend to be the superior soil removers, this can limit the cleaning ability of the quat-containing formulation. One formulator claims that by formulating with an

ethoxylated amine the ethoxylation gives greater water solubility [49], but this is an exception to the rule.

Weak organic acids can be used to disinfect bathroom surfaces which is especially useful because of the ability of acids to remove to soap scum and hard water deposits. Examples of the acids claimed for this use include lactic, citric, or glycolic [50,51]. It can be seen from this list that acids used as disinfecting agents are generally organic buffering acids of chain lengths between four and six carbons. They may either have hydroxyl groups or not. They are usually used in the range of 0.5–5%.

An interesting recent trend is the use of natural plant oils (sometimes based on folk knowledge) as disinfecting ingredients. Many formulations do not use the plant oil as the exclusive means of disinfection, mixing the oils with peroxide [52–54] but there are exceptions [55–57]. Pine oil cleaners might be considered the original prototype for this type of disinfectant but pine oil was primarily added for its cleaning ability.

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Five-Membered Heterocycles

Vishnu Ji Ram, ... Ramendra Pratap, in The Chemistry of Heterocycles, 2019

Ring Transformation of Heterocycle

t-Butyl hypochlorite oxidation of 5-aryl-6-substituted-3,6-dihydro-2*H*-1,3,4-thiadiazin-2-one led to yield thiadiazine dioxide, which on hydrolysis yielded 4-aryl-5-substituted-1,2,3-thiadiazole with loss of CO₂ and water.949



4-Benzyl-5-methyl-1,2,3-oxadiazole has been transformed950 to 4-benzyl-5-methyl-1,2,3-thiadiazole on reaction with ammonium hydrosulfide and H₂S in ethanol at 5–10°C for 24 h.



5-Aroyl-3(2*H*)-isothiazolones on reaction with hydrazine or semicarbazide hydrochloride underwent ring transformation to 4-aryl-5-(*N*-substituted carboxamido)methyl-1,2,3-thiadiazoles.951



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Hydrogenation and Corrosion Investigations of Titanium Under Attack by an External Cathodic Current

Joseph Riskin, Alexander Khentov, in Electrocorrosion and Protection of Metals (Second Edition), 2019

12.3.2 Two Corrosion Mechanisms of Hydrogenated Titanium

The effect of the hypochlorite content on the corrosion rate was studied at potentials -0.4 and -1.0 V. These potential values were chosen because the first (corresponding to the maximum corrosion) lies in the range -0.2 to -0.6 V where the corrosion rate is potential-dependent, and the second is in a range where the corrosion rate is potential-invariant (Figure 12-4, curve 3). This difference may be due to diverse corrosion mechanisms. The effect of the hypochlorite content on the titanium corrosion and hydrogenation in stirred flowing solutions proved to be similar both at -0.4 and at -1.0 V (Figure 12-6). These data confirm the assumption that the corrosion proceeds through the stage of formation of the hydride; they also indicate that the decrease in the corrosion rate with the increasing concentration of hypochlorite is related to the decrease in the hydrogenation. Such behavior was observed in both the potential ranges under consideration.

Thus, the differences in the mechanisms of titanium corrosion are determined by the way in which titanium hydride is formed during the cathodic polarization and is transferred into the solution. This conclusion is supported by the fact that at $pH \le 2.3$, titanium hydride is thermodynamically unstable in the potential range from -0.2 to -0.6 V, but is stable at higher cathodic potentials [15,16]. Titanium corrosion under these conditions may result from mechanical fracture of the brittle surface layers of titanium hydride. This agrees with the above-mentioned data presented by Tomashov et al. [11]. They observed local failures of a titanium electrode with a scanning electron microscope and attributed them to chipping of the hydride layer formed at high cathodic potentials resulting from internal stresses that appear in this layer.

To verify that titanium is transferred into solution differently depending on the potential, hydrogenation and corrosion were tested side by side at -0.4 V (maximum

corrosion) and -1.0 V (the region of potential-invariant corrosion rate). Titanium specimens (preradiated in a nuclear reactor) were polarized for 30 min at -0.4 and -1.0 V in a vigorously stirred, flowing 260 g/L NaCl solution saturated with chlorine and labeled with tritium. The solutions were filtered through pores no greater than 0.5 µm in diameter; the amount of titanium collected on the filter was determined by gamma activity. The filters were then washed with 2 L of distilled water, which completely removed the tritium-labeled water (as a control experiment showed). With the help of the above-mentioned technique [14], the hydrogen content was determined in the precipitate on the filter.

Only 3% of the total amount of titanium that passed into solution was detected on the filter after polarization at -0.4 V. On the other hand, after polarization at -1.0 V, this amount was equal to 46.3%. At -0.4 V, no tritium was found in the precipitate. The tritium content in the precipitate determined at -1.0 V suggests that the ratio of the hydrogen atoms to titanium atoms retained by the filter was close to 1. This proves that at -1.0 V, titanium passes into solution not in the ionic form, but as hydride particles chipped from the surface layer of the titanium. After chipping, some of the hydride particles may dissolve, since their potential must be shifted toward the positive region, i.e., to the range of thermodynamic instability of titanium hydride.

In these experiments, the depth distribution of hydrogen in the titanium specimens after polarization was also studied. The specimens were rapidly dissolved in 40% H₂SO₄ during which the metal atoms passed into the solution, while hydrogen gas evolved simultaneously. The depth distribution of hydrogen in a sample was determined by repeating this procedure. Table 12-2 shows that for the specimens polarized at –0.4 V, the average composition of the 0.66-µm-thick surface layer was TiO_{0.12}. In the specimens that were polarized at –1.0 V, the hydrogen content was higher by one order of magnitude. The average composition of the 0.56 mm thick surface layer was TiH. Hydrogen had penetrated to a depth of 13.20 µm.

No. of Layers		Potential-0.4 V	Potentia	Potential-1.0 V	
Thickness of Layers m)	; (µ-	Average Atomic Ratio H/Ti in the Layer	Thickness of Layers (µ- m)	Average Atomic Ratio H/Ti in the Layer	
1	0.66	0.12	0.56	0.98	
2	0.56	0.10	0.62	0.92	
3	0.93	0.088	1.23	0.86	
4	0.23	0.046	0.73	0.32	
5	1.64	0.021	0.62	0.11	
6	1.89	0.09	2.17	0.068	
7	2.19	0.01	2.38	0.043	
8	_	_	3.31	0.008	
9	_	_	1.78	0.003	

Table 12-2. Penetration of Hydrogen Into Titanium Specimens

Thus, in the region of the potential where hydride is thermodynamically unstable, the corrosion of titanium is caused by the dissolution of hydride, whereas at more negative potentials it is caused by <u>embrittlement</u> of the surface and subsequent chipping of the hydride particles.

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Risk assessment of biocorrosion in condensers, pipework and other cooling system components

P. Cristiani, in Understanding Biocorrosion, 2014

15.3.2 Chlorination by-products and discharge limits

The oxidative power of both hypochlorite and hypobromite forms is not enough to reach complete degradation of organic matter dissolved into water leading to the formation of stable organic by-products. The most important ones are trihalomethanes (THMs) which persist in water with the exhaust residual oxidant (Minear and Amy, 1995). By-product production is a concern that mainly limits the extensive use of chlorination in the recommendation for risk assessment of biocorrosion.

US EPA includes CHCl₃, CHBr₃, CHClBr₂ and CHCl₂Br in THMs, since studies in the 1970s on the by-products generated by disinfecting treatments of drinking water demonstrated the toxicity of these chemicals (Jolley *et al*, 1976). Tribromomethane is formed particularly, by spontaneous reactions with organic matter after the reaction (15.1) during chlorination in seawater.

Chlorinated by-products (CBPs) comprise other organo-halogenated non-oxidising secondary products such as haloacetonitriles and compounds from their hydrolysis (ASCE/AWWA, 1990), the concentration of which is usually negligible at the discharge of industrial cooling circuits.

Bromofonns were actually detected in cooling circuits during chlorination with dosing concentrations above 1 mgL₋₁ (Jenner *et al*, 1997). Subsequent works demonstrated that chlorination treatment with oxidant concentration equal to or less than 0.2 mgL₋₁ do not give significant concentrations of halomethans (Cristiani, 2010; Khalansky, 2003). However, the use of chlorination is discouraged by regulations all over the industrialised world.

The standard limit of chlorine concentration at discharge into natural water bodies is generally now 0.2 mgL₋₁. The dosage can be continuous or discontinuous taking into account many factors including meteoclimatic characteristics of the site, cooling circuit design, water flow and biofouling typology.

As a conservative rule, the chlorine concentration is generally set in order to have less than 0.2 mgL₋₁ residual oxidant not far downstream from the condenser. In cases where it is not enough to prevent/remediate biofilm development (as in the case of Figure 15.4), a dechlorination treatment can be applied with dosages of reductants such as sodium metabisulfite or sulphur dioxide.

Dechlorination avoids the risk of exceeding the restriction imposed at discharge. Generally, there is no specific limitation at the discharge concerning the chemical reductants used. Nevertheless, attention must be paid in their dosage. Overdosages may deplete the dissolved oxygen concentration or may alter the pH of receiving streams.

In most situations, the residual oxidant concentration is not adjusted by reductants as the temperature increases in the condenser and the contact time up to discharge is sufficient to exhaust it almost completely. Another possible solution, often adopted to reduce the concentration peak of the residual oxidant in the water, exists in performing chlorination on a half condenser box in sequence.

In some geographic areas, the use of chlorine is completely banned (e.g. some sites in Italy and in the Netherlands). In those cases, the storage and generation of chlorine, as well as the dechlorination, is forbidden in the plant.

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Separation, Preconcentration and Spectrophotometry in Inorganic Analysis

Zygmunt Marczenko, Maria Balcerzak, in Analytical Spectroscopy Library, 2000

34. 2. 1 Indophenol method

The reaction of ammonia with hypochlorite and phenol in an alkaline medium (Berthelot's reaction) yields a blue product which is the basis of a sensitive and specific spectrophotometric method for determining nitrogen as ammonia [12–19]. The probable mechanism of the reaction is:

Chloramine, which is formed as the first step of the reaction, reacts with phenol to yield quinonechloramine. This reacts with another phenol molecule to give indophenol. The blue colour is due to the indophenol anion, formed in alkaline medium. The intensity of the blue colour is greatly increased by adding a little acetone (~ 0. 2 ml of acetone per 25 ml of solution). The molar absorptivity at $\Box_{max} = 625$ nm is 4. 5–103 (a = 0.32).

The indophenol can be extracted with isobutyl– or isoamyl alcohol after adding a considerable amount of sodium chloride to the aqueous solution as a salting–out agent. The organic extract is, however, less intensely coloured than a corresponding solution in aqueous acetone [20]. The reaction is similar if thymol is used instead of phenol [21,22].

Ammonia is usually determined after being separated from a strongly alkaline medium and then absorbed in dilute H₂SO₄ or HC1. It is sometimes possible to carry out the indophenol reaction without separating the ammonia (*e. g.*, in natural waters). In the presence of EDTA, moderate quantities (0. 1–0. 5 mg) of Ca, Mg, and Al do not interfere. The addition of tartrate prevents the precipitation of hydrolysable metals. Phosphate interferes in the colour reaction [23].

Since the sensitivity of the method is often limited by the high blank values caused by the presence of traces of ammonia in the reagents, purification of the reagents by distilling ammonia from their alkaline solutions may be necessary.

Reagents

Phenol–acetone solution. Dissolve 70 g of phenol in 15 ml of ethanol, add 20 ml of acetone, and dilute the solution with ethanol to 100 ml.

Sodium phenolate solution. Immediately before use, mix 10 ml of the phenol–acetone solution with 10 ml of 30% aqueous NaOH solution, and dilute with water to 50 ml.

Sodium hypochlorite, 2% solution. (Check the content of CIO– in the solution iodometrically).

Standard ammonia solution: 1 mg NH₃/ml. Dissolve 3. 1410 g of ammonium chloride (previously dried at ~ 100°C) in water, and dilute the solution with water to 1 litre in a volumetric flask.

Standard ammonia solution: 1 mg N/ml. Prepare as above but with 3. 8190 g of dried NH₄Cl.

Sodium hydroxide: 30% aqueous solution. Boil the solution for 10–15 min in an open vessel to remove traces of ammonia.

Procedure

*Distillation of NH*₃. Place the sample solution containing ammonia in a 70–150 ml still. Immerse the condenser outlet in a receiver containing 5 ml of water and 5 drops of 0. 1 *M* H₂SO₄. Pour 10–20 ml of 30% NaOH into the still, and dilute with water to 40–80 ml. Add a few fragments of porous porcelain to promote regular ebullition, and distil a quarter of the liquid volume from the still into the receiver.

Determination of NH3. Place all or part of the distillate, containing not more than 40 ng of NH3, in a 25-ml standard flask. Add 2. 5 ml of the sodium phenolate solution and 1 ml of the sodium hypochlorite solution. Dilute the solution to the mark with water, and mix thoroughly. After 30 min, measure the absorbance at 625 nm against water (or a reagent blank solution when traces of ammonia are being determined).

Note. For determination of traces of ammonia, the sample solution should be made slightly acidic with 0. 5 ml of 0. 1 *M* H₂SO₄, and concentrated by evaporation, before the distillation.

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