OXIDATION

GE 2

Oxidoreducing reactions are those which use:

- losses (oxidation) or gains (reduction) of electrons by some ions,
- losses or gains of oxygen atoms by other ions,
- transformation into water and CO_2 (and sometimes into nitrogen) of undesirable organic materials.

While reduction reactions limit themselves, most often in practice, to eliminating dissolved oxygen and changing the toxic hexavalent chromium into less toxic trivalent chromium, oxidation reactions are used in numerous applications:

- disinfection,
- changing soluble compounds into insoluble compounds easily removable by filtration (iron, manganese),
- changing unwanted compounds into acceptable compounds (phenols, nitrites, ammonia),
- and of course, biotechnology-based processes.

Air ventilation oxidation

An abundant and cheap reactant, the air oxygen is the more widely used oxidising agent in iron removing techniques.

Placing water in contact with air makes it possible to dissolve the atmospheric oxygen. This dissolved oxygen yields a low oxidising power, nevertheless sufficient to change at ambient temperature the mineral iron present in the Fe^{2+} form (ferrous iron) into Fe^{3+} (ferric iron), whose compounds (oxide and hydroxide) are very little soluble.

Oxidation by chlorine and chlorine derivatives

The Cl_2 formulated chlorine reacts with water to initially yield hypochlorous acid as per the reaction:

$$\underset{\textit{chlorine}}{Cl_2} + \underset{\textit{water}}{H_2O} \rightarrow \underset{\textit{hypochlorous acid}}{HClO} + \underset{\textit{hydrochloric acid}}{HCl}$$

In a second step, the hypochlorous acid will be ionised into hypochlorite ions according to the reversible reaction:

$$\underset{\textit{hypochlorous acid}}{HClO} \Leftrightarrow H^+ + \underset{\textit{hypochlorite ion}}{ClO^-}$$

Chlorine acts upon numerous organic materials to change them into water, CO_2 and possibly nitrogen.

The oxidising effect on organic materials (dissolved or colloidal) and the biocide action upon bacteria is maximum when chlorine is in its hypochlorous acid form (HClO).

The amount of chlorine in hypochlorous acid form (also called "free active chlorine") is highly dependent on the pH as shown in the following table.

The following table shows the pH control and adjustment importance in processes based on chlorine and chlorine derivatives.

pH	**% chlorine in HClO form (free active chlorine)**
6	95
6.5	90
7.0	70
7.2	60
7.4	50
7.6	40
7.8	30
8.0	20

Table - Changes in active chlorine contents as a function of the pH

Chlorine action on ammonia and aminated compounds

With ammonia and aminated compounds, and depending on the pH and chlorine contents, the chlorine may produce either nitrogen or chloramines.

For pH percentages higher than 7.7 or when the chlorine contents is not high enough, the reaction leads to the production of chloramines. Despite of their bactericide power, chloramines are very little oxidising and feature the disadvantage of providing water with unpleasant properties (taste and smell, high mucosa irritation).

Gaseous chlorine

This is the most economical state for chlorine use. However, chlorine is a highly toxic gas. Specific precautions must be taken concerning storage (special premises with ventilation, heated in winter and equipped with a leak detector) and handling (no intervention by a single person, gas mask at hand's reach, goggles).

Sodium hypochlorite ("Javel water")

"Javel water" is one of the most widely used disinfectants because of its very high availability and low cost.

In its concentrated form, (47/48 chlorometric degrees), Javel water is:

- heavily loaded in chlorine (about 150 g chlorine per litre),
- easy to handle,
- injectable via metering pumps with or without dilution,
- easy to preserve away from heat and light,

but on the other hand:

- it generates vapours that are corrosive for metallic environments,
- is a highly alkaline reaction product (containing free soda) which leads to deposits at the injection point and when the water to be treated is substantially hard (TH greater than 8 - 10°f),
- for the same reasons, generates undesirable deposits in the reactive tank of the metering unit when the dilution water has not been softened,
- introduces a substantially strong alkalinity, which in some cases may require a pH correction by adding acid reactants,
- is unstable in diluted solutions (less than 2%) and should be used within 48 hours in such a case.

Calcium hypochlorite (Lime chloride)

Also called "lime chloride", the calcium hypochlorite is a solid product containing a high proportion of chlorine (more than 90%), very stable when stored in a dry and cool place.

Easily soluble in water, it is easy to use and due to its neutrality, generates no alkalinity.

The calcium chloride results in significantly increasing water hardness when it is used in great proportions.

Chloro-isocyanates

Solid products featuring high chlorine contents (60 - 90%), stable when stored in dry, cool places, the chloro-isocyanuric family compounds are marketed under several forms:

- powders, granulates or quick dissolving pellets (Permochlorine, Permoactif),
- slow dissolving pebbles (Permoseptil).

These non alkaline products do not significantly change the pH at normal utilisation doses.

The main scope of application of this family products encompasses swimming-pools, decorative ponds and fountains.

In this application, chloro-isocyanates override other chlorinated products in that they can be stabilised (breakdown under the action of slowed sunlight) by adding some isocyanuric acid which is then called "stabiliser" (PermoAX).

Quick dissolving chloro-isocyanates should never be dissolved before use, because any concentrated solution instantaneously generates a high amount of gaseous chlorine. Therefore, these products are always operated by direct manual introduction into the pool to be treated.

Only slow dissolving pebbles may be used with metering systems (so-called "pebble metering systems"), subject to a nearly continuous operation.

Chlorine dioxide

Formulated ClO_2, the chlorine dioxide is produced in situ by making sodium chlorite react with hydrochloric acid:

$$5\ NaClO_2 + 4\ HCl \rightarrow 4\ ClO_2 + 5\ NaCl + 2\ H_2O$$

This slow reaction requires acid in excess to be complete.

The chlorine dioxide is preferred to chlorine and other chlorine compounds when the water to be treated contains phenol traces, which in presence of chlorine make up chlorophenols at the origin of unpleasant tastes.

Electrochlorination

The electrochlorination process consists in on-site producing of chlorine by electrolysis of a rich solution of sodium chloride.

Making up this brine requires the use of softened water, otherwise electrolysis cell cathodes (generating OH- ions) might rapidly become scaled.

Bromine oxidation

Bromine is a less powerful oxidiser than chlorine, which features antiseptic and bactericide properties within a wide pH range (up to 8.2). It is mainly used in sea water swimming-pools, that are always slightly alkaline.

Bromine is operated as bromine water made up on site by paddling water in liquid bromine, or by reaction between an alkaline bromine and an oxidiser more powerful than bromine (chlorine, hypochlorite, ozone).

Ozone oxidation

Ozone (formulated O_3) is a very unstable allotropic variant of oxygen which easily breaks down into molecular oxygen and incipient oxygen:

$$\underset{\text{ozone}}{O_3} \rightarrow \underset{\text{molecular oxygen}}{O_2} + \underset{\text{incipient oxygen}}{O}$$

The incipient oxygen released in this way is one of the most powerful oxidisers whose oxidising, discolouring, algaecide, bactericide and viricidal properties are noticeable. The decaying phase generates no toxic by-product.

On the other hand, it is a toxic gas, the residual traces of which must nearly always be destroyed on treatment completion.

Destroying residual ozone

Ozone can be eliminated:

- chemically: by mixing in a solution of reducing reactive (bisulphite) for small size facilities,
- by catalytic process (active carbon column periodically renewed) for average size facilities,
- by thermal process for large size facilities,
- by UV radiation.

Compatibility of materials with ozone

The ozone oxidising power applies not only to undesirable impurities contained in water, but also to materials that are in contact with ozone enriched water.

Oxidation by peroxide compounds

As for ozone, peroxide compounds (hydrogen peroxide, potassium permanganate, persulfuric acid, peracetic acid) release incipient oxygen and as such, are used as oxidising and disinfecting agents.

Hydrogen peroxide

Formulated H_2O_2, the hydrogen peroxide breaks down into water and incipient oxygen:

$$H_2O_2 \rightarrow H_2O + O$$

Its decomposition is faster under alkaline pHs than under acid pHs, and produces no other product but water.

Therefore, the hydrogen peroxide does not change treated water salinity.

Residual hydrogen peroxide traces spontaneously disappear after some time. Washing apparatuses, tanks and pipes then becomes very easy.

Its cost restricts its applications to treatment of demineralised waters and facilities from which any reactant trace is banned (e.g., medical and pharmaceutical engineering demineralised water piping systems, ultra-pure water in the electronic components industry).

Peracetic acid

Under the designation of peracetic acid, a mixture of water, acetic acid (CH_3COOH), hydrogen peroxide (H_2O_2) and peracetic acid (CH_3COOH) is marketed.

The hydrogen peroxide oxidising power is supplemented by the peracetic acid oxidising power and the acetic acid disinfecting power. This is why the peracetic acid is mainly used as disinfecting agent.

The peracetic acid oxidising activity is nearly not influenced by the pH.

Potassium permanganate

Formulated $KmNO_4$, the potassium permanganate breaks down into oxygen, potassium salts and manganese oxide. Its main applications are:

- disinfection of water distribution networks for human consumption: the strong pink coloration it provides to water under low contents facilitates control by mere visual inspection,
- oxidation of manganese dissolved into insoluble oxide which can be easily filtered on calcareous material.