The State of Art in the Use of Chlorine Dioxide and Ozone in the Treatment of Water

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Abstract

The paper presents the basic ideas of practical developments in the use of oxidants at the Brussels' Intercommunal Waterboard (CIBE) where an important raw water treatment plant, receiving water from the river Meuse, was designed and constructed.

The CIBE has put into operation part of this plant of which the final design capacity will be 260 000 m^3/d. The water is treated by oxidation (ClO_2 + Cl_2), coagulation, adsorption, flocculation, settling, stabilisation, sedimentation, filtration and ozonation. The drinking water produced is mixed with various groundwaters impounded by the Company. Therefore, a reliable plant capable of delivering a water of comparable quality with that of the groundwater, was constructed. Designing the plant required more than two years of intensive preparatory investigation on the most appropriate chemical and physical processes. The optimisation of these processes was achieved by the correct choice of treatment and the major developments discussed in this paper are the theoretical and practical studies of the use of ClO_2 as well as the development of ozonation processes.

Introduction

The disinfecting properties of chlorine dioxide used in water have been known since the beginning of the century although it was only in the fifties that it was applied for the treatment of drinking water. The need for disinfectants other than the less expensive chlorine, has been proven from time to time. It is e.g. well-known that the extensive use of Cl_2 promotes the formation of chlorophenols which cause an unpleasant taste and odour.

In the case of ozone which was discovered in 1840 its strong disinfecting power was already well established at the turn of the century. In 1904 the city of Nice in France decided to ozonise its water and this operation was started in 1906 and later successfully extended.

There is an increasing interest in the techniques of oxidation of dissolved compounds in drinking water as well as in wastewater. The formation of possible toxic chlorinated compounds with chlorine appears to be the major reason for this interest.

Arguments against the introduction of ozone include costs, instability of the reagents, risks associated with handling, lack of specific analytical methods especially for residual concentration analyses and sometimes also possible consequences of unknown facts. In the case of chlorine dioxide, the possible presence of the chlorite ion in treated water was sometimes raised as an objection since a suitable analytical method for its detection was not available. For ozone, the instability of the residual compound (not allowing permanent post-disinfection) and problems associated with aftergrowth were advanced.

Among the different reactions which occur between chlorine dioxide or ozone and dissolved organic products, are oxidised products. Particularly with ozone, these transformations are biological degradations, and consequently these techniques release "more natural", hence more metabolisable oxidised products, than in the case of treatment with chlorine (Masschelein 1969, 1975, 1979a; Rice and Cotruvo, 1978).

Pure chlorine dioxide applied for 40 to 60 min to raw water does not release trihalomethanes and is even capable of destroying the precursors to the formation of these volatile chlorination — bromination products. Oxidation of bromide to bromine is theoretically in equilibrium with the reduction of chlorine dioxide to chlorite (Levi and Perotti, 1958).

In 1968, the CIBE decided to produce a complementary amount of treated surface water to be added to the groundwater and the systematic use of chlorine dioxide was progressively introduced in addition to the chlorination-post-ammoniation process already in use by the Company for more than 35 years. This combination is necessary to mix the different waters without the risk of bacterial aftergrowth. The decision necessitated at that time more than two years' preliminary documentary investigations, research in the laboratory as well as technical developments. At present, the processes remain under permanent investigation under practical conditions as waters from several different sources are mixed and chlorination is repeated after the chlorination- post-ammoniation of the groundwaters.

More about the scope and limitations of the use of these chemicals are discussed in previous reviews by the author (1975, 1977 and 1979a), and will not be discussed in detail in this paper.

Generation of the Oxidants

Chlorine dioxide and ozone are both unstable gases which require generation on the site of their use. Concentrated solutions of chlorine dioxide (0,5 to 3 g/ℓ) may be stored for a few hours before application.
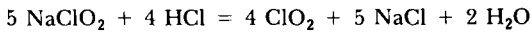
Chlorine dioxide

The reactions that enable practical synthesis of chlorine dioxide on a scale needed for the treatment of drinking water are:

$$2 \text{ NaClO}_2 + \text{Cl}_2 = 2 \text{ NaCl} + 2 \text{ ClO}_2$$

and

$$5 \text{ NaClO}_2 + 4 \text{ HCl} = 4 \text{ ClO}_2 + 5 \text{ NaCl} + 2 \text{ H}_2\text{O}$$

Methods of preparation starting from the chlorates are not practical since they generally require a production capacity much higher than that needed for the treatment of drinking water. Production capacities of 1 t/d have been described as being the lowest limit of yield of the chlorate processes (Masschelein, 1969). Oxidation of chlorite with persulphate is practically limited to the disinfection of swimming pools:

$$2 \text{ ClO}_2^- + \text{S}_2\text{O}_8^= = 2 \text{ ClO}_2 + 2 \text{ SO}_4^=$$
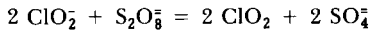
In the synthesis of chlorine dioxide starting from chlorite and chlorine, a minimum chlorine concentration is necessary to enable the formation of chlorine dioxide without interfering reactions, such as reactions releasing chlorates:

$$6 \text{ ClO}_2 + 3 \text{ H}_2\text{O} = 5 \text{ HClO}_3 + \text{HCl}$$
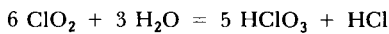
At initial chlorine concentrations of 0,4 to 0,5 kg/m^3 equal weight proportions of chlorine and sodium chlorite are necessary. This is equal to an excess of 200 to 250% in chlorine. At an initial chlorine concentration of 1 to 1,5 kg/m^3 the yield amounts to 90%, the final pH being between 4 and 5. At higher initial chlorine concentrations (up to 3 kg/m^3) the reaction occurs stoichiometrically, the final pH being 5 to 8. Under these conditions the final chlorine dioxide concentration exceeds 6 kg/m^3. At these concentrations a dilution of the stock solution is necessary for safety reasons. For proper operation conditions, adequate security measures are necessary, such as:

● suitable equipment to control the dosage of sodium chlorite when there is a shortage of chlorine or feed-water;

● the presence of a diluting zone in the reactor where the preparation of concentrations are possible, and considered safe before injection to the effluent;

● the adequate ventilation of eventual storage;

● and the insulation for the prevention of fire of all electrica connecting systems.
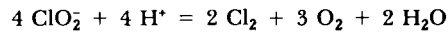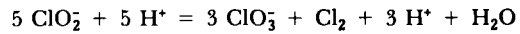
A reactor for the preparation of ClO$_2$ from NaClO$_2$ anc Cl$_2$ is installed at Spontin-Zienne and similar reactors are instal led in the Tailfer plant and are each capable of producing ClO of up to 7,5 kg/h. They have been in operation for more than £ years on a continuous basis applying direct dosing without intermediate storage of the concentrated solution.

As the final pH value is acid the direct use of sodium ol calcium hypochlorite for the oxidation of chlorite is not a possible technique unless catalysts are present (Masschelein, 1967). The cost of these processes make them suitable only for laboratory application.

In smaller plants the use of chlorine in gas phase may cause problems associated with the safety of storage and operation of liquified chlorine. This is the reason why the hydrochloric acid process is sometimes used.

The direct reaction between sodium chlorite and hydrochloric acid at dilutions capable of forming chlorine dioxide at concentrations of 0,5 to 2 g/ℓ, gives yields of only 60 — 80 % calculated on the starting chlorite (Masschelein, 1979a). Several secondary reactions can lead to the formation of chlorine:

$$5 \text{ ClO}_2^- + 5 \text{ H}^+ = 3 \text{ ClO}_3^- + \text{Cl}_2 + 3 \text{ H}^+ + \text{H}_2\text{O}$$

$$4 \text{ ClO}_2^- + 4 \text{ H}^+ = 2 \text{ Cl}_2 + 3 \text{ O}_2 + 2 \text{ H}_2\text{O}$$

The chlorous acid can disproportionate according to:

$$4 \text{ HClO}_2 = 2 \text{ ClO}_2 + \text{HClO}_3 + \text{H}_2\text{O} + \text{HCl}$$
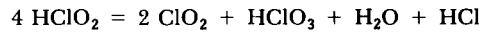
The yields (up to 100 % in the case of ClO$_2$) depend on the design of the mixing zone of the reagents in the reactor. The results anticipated were obtained when working with an inverted contact chamber of conical shape enabling tangential entries of reagents (Belgian Patent 757,426; 1971).

The best way to activate the reactor is by maintaining a state of sufficient depressure. This is possible with an ejector which sucks in dioxide simultaneously in a gaseous and liquid state. Should the ejector have a shortage of dilution water or should the depressure become insufficient, the reactor must stop immediately. This operation must be automated to ensure the security of the whole process.

Other precautions, such as ventilation of the premises and fire-protection where chlorite is stored, are similar to those provided in the case of chlorite-chlorine reactors.

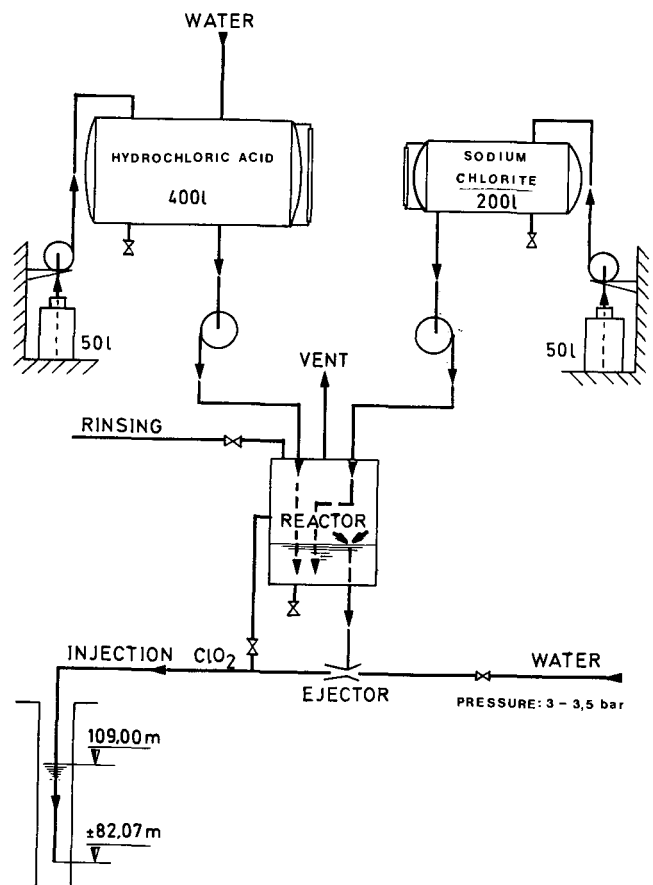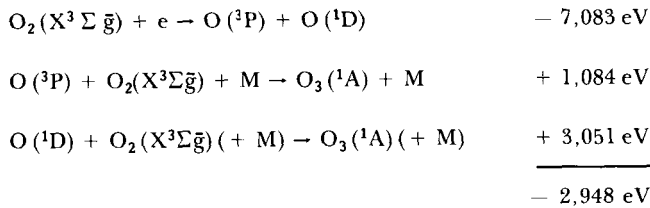See Fig. 1 for the preparation of ClO$_2$ from NaClO$_2$ and HCl at the Martin-Villeret plant.

Figure 1
Preparation of ClO$_2$ starting from NaClO$_2$ and HCl at the St-Martin-Villeret plant
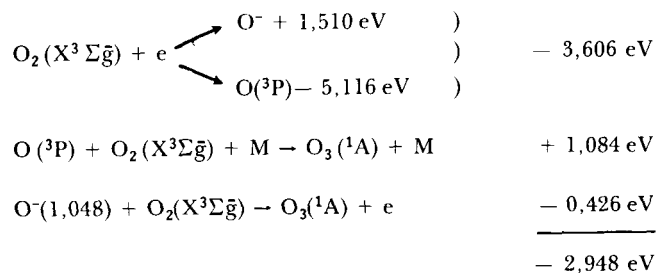
Ozone

Ozone can be formed by several ways which have been reviewed previously (Masschelein, 1977). The corona discharge method using a dry, dust-free gas containing oxygen, is the most practical method for use in water treatment plants.

The process is based on the dissociation of oxygen releasing atomic oxygen of two different energy levels: ^3P and ^1D respectively 5,1 and 7,1 eV higher than the fundamental molecular oxygen. The internal energy of ozone in the ground state (^1A) amounts to 1,47 eV or 34 kcal/mol higher than the corresponding oxygen. A first mode of formation of ozone is as follows:
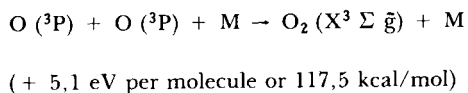
$$O_2(X^3\Sigma\tilde{g}) + e \rightarrow O(^3P) + O(^1D) \qquad - 7,083\,eV$$

$$O(^3P) + O_2(X^3\Sigma\tilde{g}) + M \rightarrow O_3(^1A) + M \qquad + 1,084\,eV$$

$$O(^1D) + O_2(X^3\Sigma\tilde{g})(+M) \rightarrow O_3(^1A)(+M) \qquad + 3,051\,eV$$

$$\overline{\qquad\qquad - 2,948\,eV}$$

Hence, the maximum possible yield is the production of two molecules of ozone per 2,95 eV. However, with the O^3P a less probable triparticular encounter is necessary.
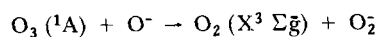
Among the other possible processes in the discharge, the ionic reactions involving the O^- of 1,084 eV should be mentioned.

$$O_2(X^3\Sigma\tilde{g}) + e \nearrow \begin{matrix} O^- + 1,510\,eV &) \\ &) \\ O(^3P)- 5,116\,eV &) \end{matrix} \qquad - 3,606\,eV$$

$$O(^3P) + O_2(X^3\Sigma\tilde{g}) + M \rightarrow O_3(^1A) + M \qquad + 1,084\,eV$$

$$O^-(1,048) + O_2(X^3\Sigma\tilde{g}) \rightarrow O_3(^1A) + e \qquad - 0,426\,eV$$

$$\overline{\qquad\qquad - 2,948\,eV}$$

A series of reactions in the discharge zone can form ozone of + 1,47 eV per molecule. However the maximum possible energy efficiency is not higher than 50 % of that of theoretical efficiency. Moreover, transient radicals and ions formed during the discharge can return to the state of oxygen as is given in the following reactions:

$$O(^3P) + O(^3P) + M \rightarrow O_2(X^3\Sigma\tilde{g}) + M$$

(+ 5,1 eV per molecule or 117,5 kcal/mol)

and

$$O_3(^1A) + O^- \rightarrow O_2(X^3\Sigma\tilde{g}) + O_2^-$$

(net energy balance: + 2,98 eV per molecule or 68,7 kcal/mol without any activation energy required).

An ozonator is to be considered as a chemical reactor operated at a steady state by a series of counteracting processes: — activation — deactivation of oxygen — thermal and photochemical decompositions (Masschelein, 1977).

The overall result of ozonators operated with air is that about 15 Wh (Watt hours) are necessary to produce 1 g ozone. This is equal to an energy yield of less than 5 %. Consequently further research is required to improve the technical production

of ozone. Most of the energy is lost as heat, and the thermal decomposition of the ozone in the discharge zone is always critical. Hence it is essential to supervise the cooling. Only 10 % of the excess heat is removed by the air flux and the temperature of the exit gas containing the ozone should normally not exceed 25°C, however 40° C is the extreme limit. Consequently the availability of cooling water is essential when using ozonators.

The most widespread ozonators at present are those with dielectrics in tubular form. The walls of borosilicate glass require a homogeneous thickness, the standard ranges are 1,85 ± 0,1 mm with an air gap of 3,1 mm. These ozonators can be operated at 12 to 20 kV. Standard ozone concentrations are 18 g/Nm³ (N is used in this paper to indicate "normal" conditions, i.e. at STP) air, in that case the energy consumption is approximately 17 Wh/g. In Figure 2 the effect of ozone concentration on the energy costs of production is given.

Increasing the production capacity is possible by enriching the oxygen content of the process gas as e.g. given in Figure 3 for the classical tube ozonator.

It is important to compare the increase in yield with oxygen enriched air when using the equipment at nominal capacity so as to avoid an over-estimate of the increase in production due to the oxygen enrichment (Masschelein, et al., 1976).

Some new types of ozonators have been designed for the use of oxygen rich process gas obtained by the pressure-swing generation method (Rosen, 1972) and recycling of the gas after contact with the water.

Design Parameters for Production Capacity

In potable water the maximum possible residual chlorine dioxide causing neither taste nor unpleasant odour ranges between 0,4 and 0,5 g/m³. This concentration is also below the admissible toxicity limit for rats where no indication of serological toxicity was obtained even at doses of 5 g/m³ (Fridlyand and Kagan, 1971). In Belgium the maximum allowable concentration of chlorine dioxide in public water is 0,25 g/m³.

When comparing the cost of post-disinfection by chlorine dioxide with that obtained when using chlorine, it has been shown that the former cost is 1,2 to 1,7 times higher than the latter (Bognolesi, 1953 and Gomella, 1961). However, the relative cost of the raw water treatment may vary significantly according to local parameters and cost ratios of 1:1 to 1:4 have been reported (Doroling, 1974). At the raw water treatment plant of the Brussels' Intercommunal Waterboard at Tailfer the treatment is carried out with both chlorine and chlorine dioxide, with comparative costs in the range of 1:1 to 1:2 and occasionally 1:4.

The use of chlorine dioxide may be an alternative to prechlorination. It has the advantage of forming little organochlorinated derivates considering the reactivity of organic derivates with this oxidant (Masschelein, 1979a). Furthermore, chlorine dioxide forms very little simple chlorinated hydrocarbons of the chloroform type (Vilagines et al., 1977 and Masschelein, 1979b).

Another advantage which is often decisive is that chlorine dioxide does not react with dissolved ammonia. It is therefore not necessary to apply higher doses than that required to obtain a "breakpoint" for a satisfactory disinfection. This is a very important point where swimming-pool water treatment is concerned.

Like ozone, chlorine dioxide has a micellizing effect in the pretreatment of water for coagulation-flocculation. Thus, the
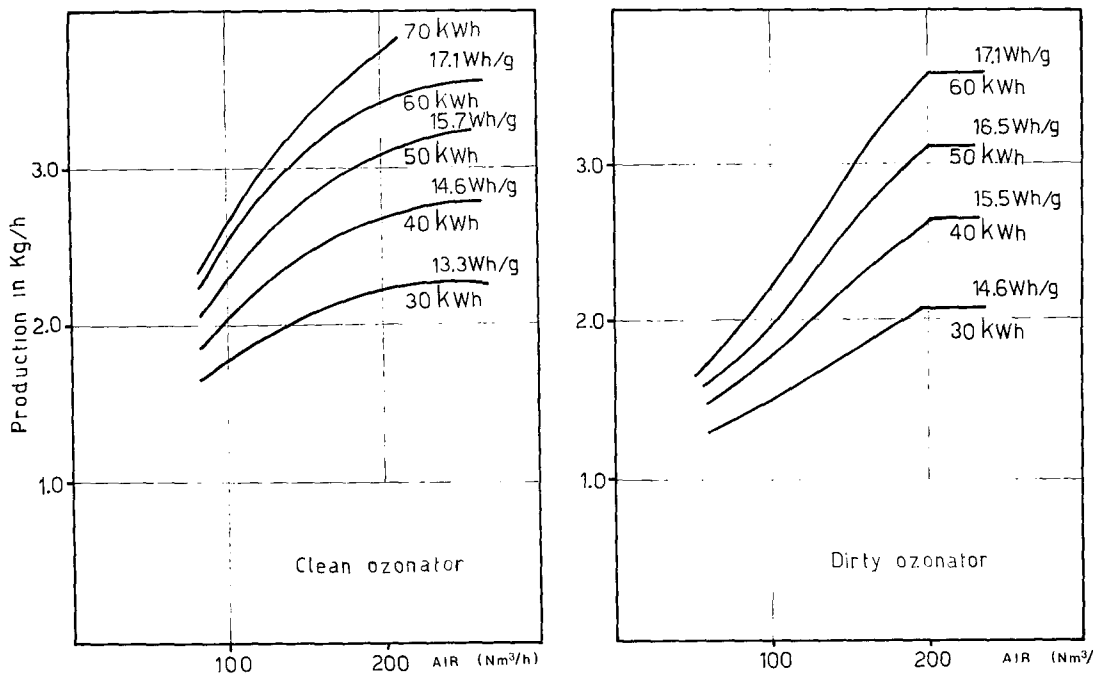
Figure 2
Effect of ozone concentration on the energy costs of production
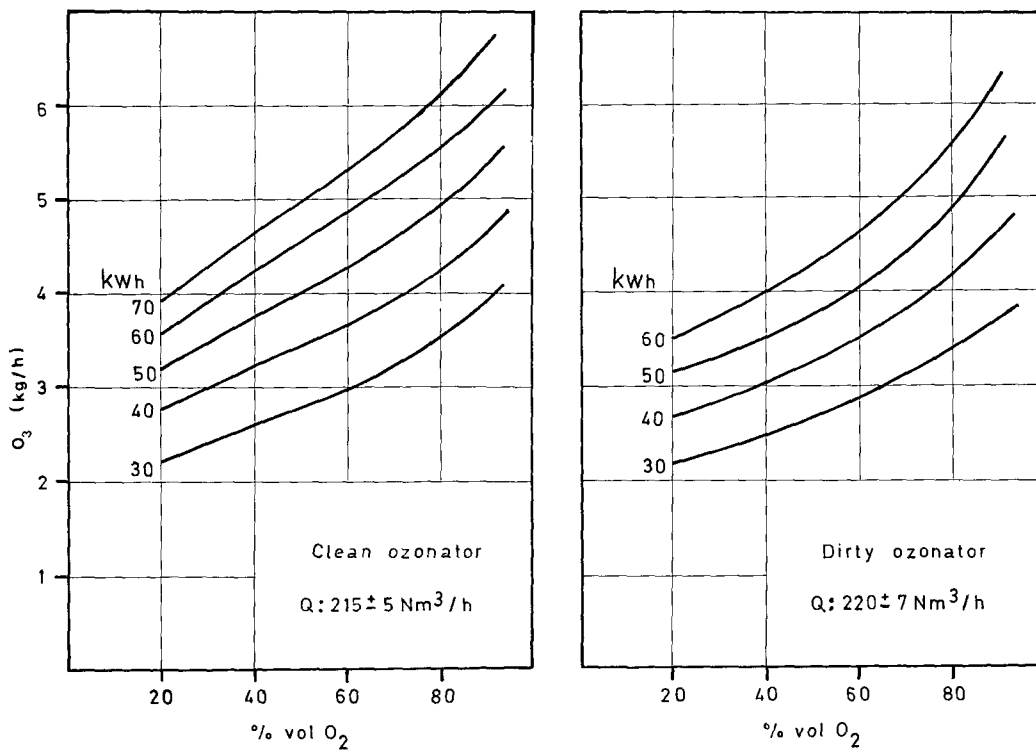

Figure 3
Increase of ozone production by the use of oxygen enriched air

turbidity of swimming-pool water treated with chlorine dioxide is lower than that obtained when chlorine is used (Bandi, 1967). Furthermore, iron and manganese present in a reduced or complexed state, particularly by fulvic or humic acids, are oxidised and eliminated by a subsequent precipitation.

In post-ozonisation the minimum practical quantity to be injected into the water is in the order of 0,5 to 1,5 g/m^3. Phenomena similar to the breakpoint in chlorination have not been reported where ozonisation is concerned. Occasional data obtained from the treated water of the River Meuse at the Tailfer Station are reported in Figure 4. However, the practical ozone demand can be subject to important seasonal variations as indicated in Figure 5.

The general criterium in post-ozonisation is to ensure a residual concentration of 0,2 to 0,4 g/m^3 after a minimum of 10 min reaction time. This level of treatment is necessary to guarantee a sufficient action against viruses. In the practice of post-ozonisation in a moderate climate, a production capacity attaining 3,5 to 4 g/m^3 is often required. In fact, the real needs must be set at a level resulting from practical experiments e.g. a pilot plant.

When used in pretreatment ozone can be injected into raw water sources at concentrations ranging from 2 to 8 g/m^3. As in the case for post-ozonisation, the level of treatment can vary as a function of the temperature and eventually of the pollution rate.

As the needs in ozone often vary as a function of time, a problem relating to the ideal dimensions of production capacity often arises. According to a previous analysis (Masschelein, 1977), when the production needs are variable, the following method of optimization is recommended:

● One ozonator in three must be considered as spare equipment (electrical coupling often involves three ozonators in parallel arrangement).

● Among these three ozonators, two must be capable of ensuring the necessary production when operated at 80% of their maximum capacity.

● When using air enriched with oxygen, an increase in production capacity of up to 175% of nominal capacity can be obtained.

● The experimental confirmation of the evaluation consists in establishing the possibility of meeting the maximum needs by 0,8 x 1,75, i.e. 1,4 times the maximum nominal capacity obtained with air.

Actual costs (in Belgian francs) for both possibilities to meet variable needs i.e. over-dimensioning of classical ozonators operated at 50 Hz, versus occasional enrichment of the process gas with oxygen, are given in Table 1.

Techniques for Dispersing and Dissolving Oxidants in Water

Dissolving chlorine dioxide at concentrations applicable in water treatment does not involve any problem except for the possibility of corrosion at the site of injection. Direct injection into the pipes is a convenient method. The injection in channels or basins should always be carried out below the surface of the water. Diffusers must introduce the concentrated solutions over
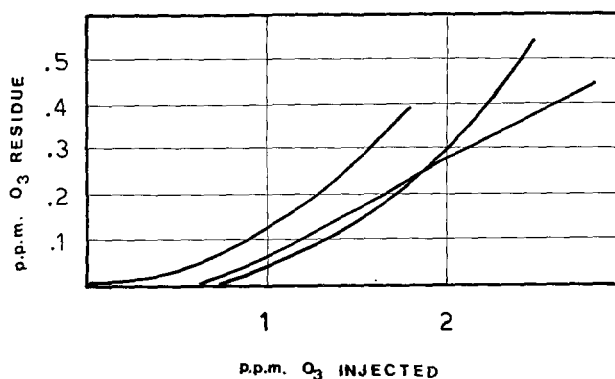

Figure 4
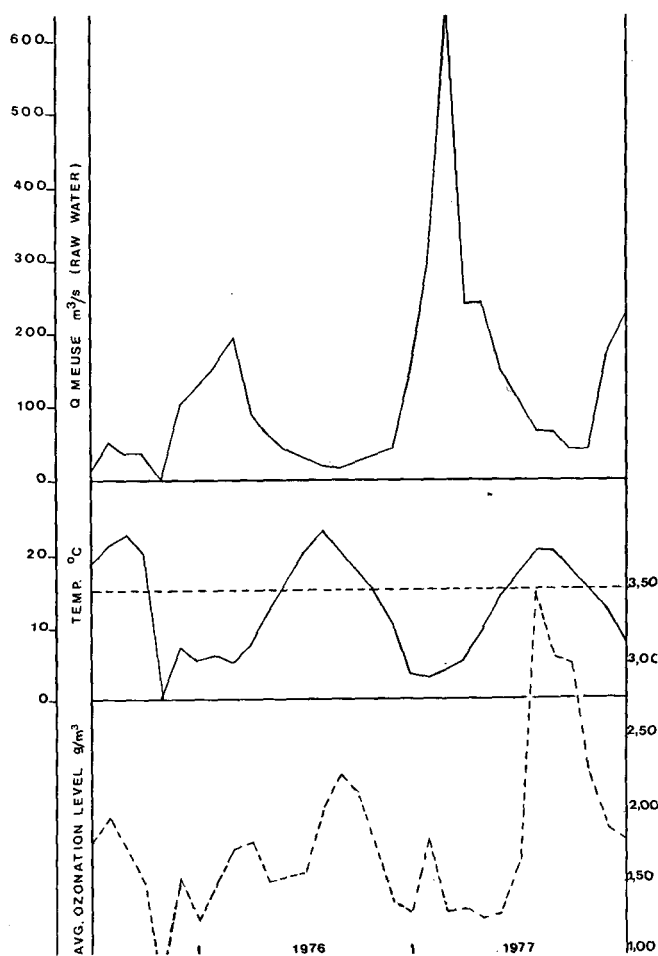Immediate ozone demand of treated river water

Figure 5
Seasonal variation of the monthly averages of ozone consumption

the whole width of the channel, preferably in a hydraulic pump. No specific contact chambers are required but the oxidant must at least be allowed to act for 40 to 60 s. The mixing energy is best kept in the range of G = 100/s to obtain instantaneous and homogeneous action.

One of the major aspects of the use of chlorine dioxide

TABLE 1
### COSTS OF OZONE PRODUCTION
(Belgian francs)

Parameter	Solution 50 Hz	Solution O_2
Premises	0,063	0,045
Equipment	0,158	0,121
Maintenance (biannually)	0,20	0,12
Energy (injection)*	0,0236	0,014
Energy (production) (1,06F/kWh)	0,04	0,025
Oxygen (4 FB/Nm³)	–	0,08
Total	0,485	0,405

*Injection by turbines
kWh = kilowatt hours
FB = Belgian francs
Nm³ = normal cubic meter
Hz = Hertz

Although the solubility of ozone in water is much higher than that of oxygen ($\pm$ 13 times more), its practical dissolution is much more difficult (Rawson, 1953). The reason for this is the low partial pressure of the ozone contained in the input gas. Direct injection into pipes is also difficult for the same reason.

Partial injection systems, in which ozonised air is sucked into a substream of the water to be treated, involve an excessive exposure of a part of the water while the greater part is not directly treated with the highly concentrated air (See Figure 6).

The substream usually represents 5 to 10% of the total flow and the method is feasible with one injection with an air to water ratio of 1:5 to 1:20. The costs are of about 2 to 3 Wh per gram of ozone for the low counter-pressure technique and 10 to 20 Wh per gram ozone for the high counter-pressure system.
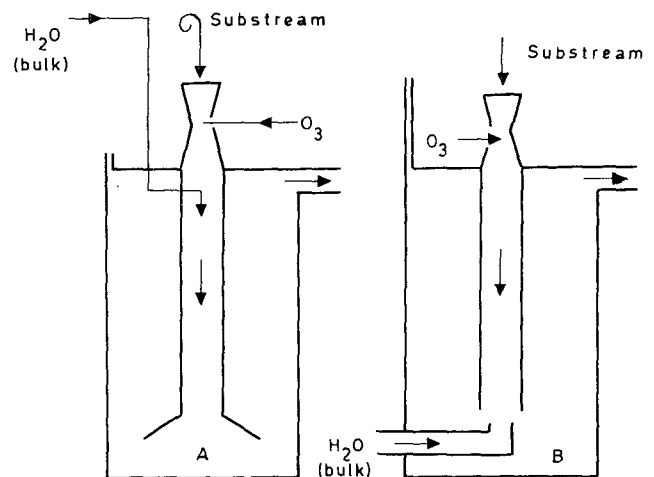

Figure 6
Partial injection systems

particularly in pretreatment of a surface or river water is the competition between the oxidation which releases chlorites and the disproportionation into chlorate and chloride.

$$ClO_2 + 1\ e = ClO_2^-$$

$$6\ ClO_2 + 3\ H_2O = 5\ HClO_3 + HCl$$
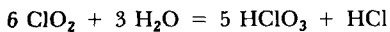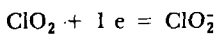
Considering these two reactions, a weight proportion of $ClO_2^-:ClO_3^-$ of 1, corresponds to 1,24 as a molar proportion. If this ratio is observed, for 6 mol of initial dioxide having reacted, 6,2 mol are lost by disproportionation. The disproportionation of the chlorite ion itself is slow in the absence of intense light. Except when submitted to intense sun-light, the following reaction may be neglected:

$$3\ ClO_2^- = 2\ ClO_3^- + Cl^-$$
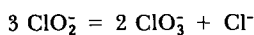
For the practical use of chlorine dioxide in the pretreatment of raw water, experience has dictated the following recommendation (Masschelein 1978, 1979a):

● a reaction time of 30 to 40 min is sufficient;

● the residual ClO_2 concentration after this lapse of time should normally not exceed 0,2 g/m³ otherwise the disproportionation part increases;

● the weight ratio of chlorite:chlorate after this reaction must be at least 1. For an open air settling tank if the residual concentration of ClO_2 exceeds 0,2 mg/ℓ the ClO_2 destruction by disproportionation to chloride and chlorates increases;

● when using chlorine dioxide in raw water pretreatment, the chlorite formed is oxidised stoichiometrically to chlorate by ozone applied in the post-treatment.

Among the total injection systems one can distinguish the total ejector, the injection through porous pipes with diffusing openings of 50 to 100 μm and spraying of washing chambers (See Figure 7). In all of these systems there is a tendency of vertical channeling of the bubbles (Masschelein, 1977) and thus a lower probability of "concentrated ozone bubble contact". The spraying or washing towers used presently are inadequate techniques if a residual concentration is to be maintained; losses range up to 30%.

Another concept than that of the "concentrated ozone bubble contact" is that of the smooth and more permanent action of a residual ozone concentration, especially for the breaking down of more resistant compounds such as alkylbenzenesulphonates and aromatic bonds when deactivated by electron capturing double bonds. This also applies to the viricidal action that cannot in any way be explained by only one of two ways of action (Katzenelson et al., 1974).

For the maintenance of a residual concentration as sole objective, the batch techniques have definite advantages.

The efficiency of the action of ozone corresponding to the different techniques of dissolution depends on the state of the substrate: dispersed and/or dissolved products.

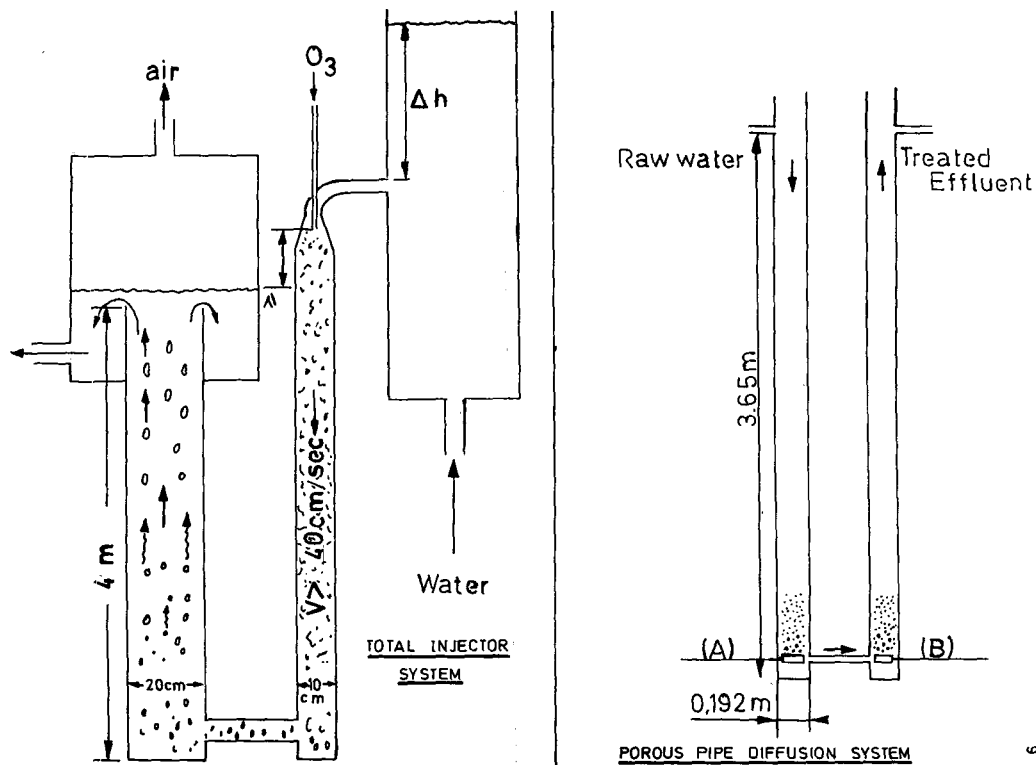On dispersed systems such as colloids in raw water or bac-

Figure 7
Pilot systems for total injection of ozone

TABLE 2
OZONATION OF FILTERED WATER (NOT PRETREATED WITH ClO_2)
(Masschelein, 1977)

Diffusion systems	ppm injected O_3	ppm residual O_3	Contact time (in min)	Actino-mycetes/ℓ	Total bacterial count/ℓ 37°C	20—22°C
Contacting tower with porous pipes	0,5	0,06	4	250	76	560
	1,0	0,2	4	20	0	220
	1,5	0,26	4	2	0	0
Chamber for water recirculation turbine	0,5	0	4	98	5	1 000
	1,0	0,05	4	0	0	0
	1,5	0,20	4	0	0	0
	2,0	0,26	(6)	0	0	0
Injection by divergent gas driving	0,8	0,12	4	40	(?)	∞
	1,15	0,16	4	(?)	36	144
	1,35	0,19	4	12	0	113
	1,55	0,31	4	0	0	0

teria, the "concentrated ozone bubble contact" is very important. The data in Table 2 illustrate this point. Besides the contact system the pH of the medium can play an important role. However, up to now, current practice has been to ozonise the water at the usual pH-value for drinking water i.e. 7 to 8.

The losses in ozone in one single injection phase range between 5 and 35 %. As a general rule:

● the higher the residual concentration, the higher the losses,

● the higher the inlet concentration, the higher the residual concentration without any direct incidence on the losses.

In selecting a contacting system, both effects should be emphasized, i.e. the promotion of an ozone-bubble contact by appropriate mixing, and the avoiding of a gas-stripping. Both should take place during a quiet period when the residual ozone dissolves in the water. Generally, the contactor for dispersing ozone in water is best selected after a pilot plant study of the problem under consideration. The choice of a system must be considered in the context of the whole plant.

Different methods of dispersing and dissolving ozone in water have been tested as pilot or full scale experiments at the Tailfer plant (Masschelein et al., 1975—1976; Masschelein, 1977). Systems tested and costs of the unit process of dissolution are given on a comparative basis in Table 3.
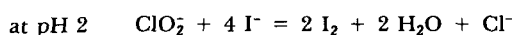
TABLE 3
COMPARATIVE OPERATION COSTS OF INJECTION
SYSTEMS. (THE COSTS ARE EXPRESSED IN ENERGY
TERMS TO FACILITATE COMPARISON)

|	
Injection through porous pipe	2 — 3 Wh/g ozone
Total injector system	4 — 5 Wh/g ozone
Rapid mixers	7 — 10 Wh/g ozone
Recirculation turbine	5 — 7 Wh/g ozone
Gas dispersor	2 — 3 Wh/g ozone
Turbine circulating water and air	5 — 6 Wh/g ozone

At the Tailfer Plant the final option was the injection of the concentrated ozonised air into the water in a first ozonisation stage of 2 min 48 s. In a pre-ozonisation stage the air escaping from the first phase is contacted with the incoming water for 2 min 34 s. Both injections are obtained by self-aspirating water/air circulation turbines. After the injection, a contact time of 6 min 7 s is carried out in baffled chambers. The ozonisation is performed at the final stage of the treatment and the residual ozone concentration required after the contact times mentioned above, is set at 0,3 — 0,4 g/m^3. The losses at the chimneys are below 1 % of the injected ozone.

Analysis of Chlorine Dioxide and Ozone

Iodometry still remains the sole practical method for the absolute determination of chlorine dioxide, and chlorite. The reactions are:

at pH 7 $2 ClO_2 + 2 I^- = I_2 + 2 ClO_2^-$

at pH 2 $ClO_2^- + 4 I^- = 2 I_2 + 2 H_2O + Cl^-$

However, chlorine is the most significant interfering reagent often encountered in practice simultaneously with chlorine dioxide. Thus, the iodometric method is merely suitable for standardisation techniques. The literature often mentions a stage to overcome interferences, principally of chlorine, by introducing a disproportionation in the reaction schemes. This is based on the reaction of chlorine dioxide:

$$2 ClO_2 + 2 NaOH = NaClO_2 + NaClO_3 + H_2O$$
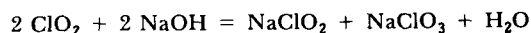
Hence, by measuring the difference before and after the disproportionation one could estimate the concentration in chlorine dioxide. However, it has been observed that in ternary mixtures $Cl_2 - ClO_2 - ClO_2^-$ (Masschelein 1969) crossed or mixed disproportionations occur. The results of this technique indicated that less oxidant should be used as given in theory and that more than the estimated concentration of chlorine dioxide be used. This complication also raises doubts about the techniques based on orthotolidine and diethyl-p-phenylenediamine (DPD).

In neutral medium, the reaction between ozone and iodide is commonly:

$$O_3 + 2H^+ + 2 I^- = O_2 + H_2O + I_2$$
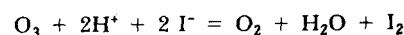
Several side reactions, such as the formation of iodate, took place (Masschelein, 1975).

The use of fritted glass gas washbottles is best avoided in the bubbling of ozonised air through the KI solution. Direct injection with a plunging glass tube or even better with the Muenke flask, is preferable so as not to destroy part of the ozone.

For the determination of chlorine dioxide in concentrated solutions such as in the reactor effluents, one can make use of the oxidation of tyrosine to dopaquinone (Hodgen and Ingols, 1954).

$2 ClO_2 + HO -\langle O \rangle- CH_2-CHNH_2-COOH =$

$O =\langle\rangle= CHCHNH_2COOH + 2 HClO_2$
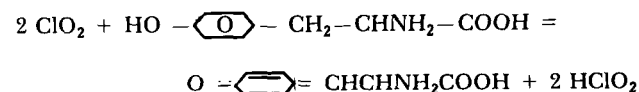
At pH 4,5 the reaction is selective for determination by absorption at 490 or 355 nm. The interference of chlorine is hardly significant if the Cl_2:ClO_2 ratio is less than 2. Ethylamine or malonic acid are possible suppressors of the interference by chlorine. The detection limit (2 σ) for chlorine dioxide of the method is 0,2 g/m^3.

Acid chrome violet K (ACVK) or 1,5-bis-(4-methylphenylamino-2-sodium sulphonate)-9,10-anthraquinone (colour index 61,710) enables the specific spectrophotometric determination of either residual chlorine dioxide or residual ozone. The reagent is discoloured at a pH of 8,1 to 8,4 obtained by an ammonium NH_3/NH_3Cl buffer. The success of the method depends on avoiding losses of the oxidant during transfer (Masschelein, 1966; Masschelein and Fransolet, 1977).

The detection limit by the usual spectrophotometric techniques is 0,04 g/m^3 for either ClO_2 or O_3. The limit of 0,02 g/m^3 can be obtained by using microcells with temperature control. The absolute significance of the ACVK method has been confirmed by spectra of the nuclear paramagnetism of ClO_2 (Knechtel et al., 1978). The dyestuff is not altered either by ozonides or by hydroperoxides.

It is often necessary to check the residual chlorite in the water treated with chlorine dioxide in post-disinfection. The

sole specific method with an acceptable sensitivity is based on a differential analysis of polarograms obtained in the pulse mode. The electrode reaction is (Hartley and Adams, 1963):

$$HClO_2 + 4\,e + 3\,H^+ = Cl^- + 2\,H_2O$$

The method is based on the adjustment of the pH between 4,4 and 4,5 by an acetic acid, acetate and ammonium sulphate buffer (Masschelein et al., 1979a). The ClO_2 or Cl_2 are removed by stripping with nitrogen and if necessary by exchange on a strong cationic resin. The detection limit is 0,05 g/m^3 for ClO_2^-.

The ozone content in air can easily be determined by U.V. gas spectrophotometry. The working wavelength for ozone absorption is the Hartley band at 254 nm. Several monitors are available, both single and double beam spectrophotometers. The practical detection limit ranges about 10 p.p.m. by volume (Masschelein, 1975).

Detection of trace concentrations of ozone in air is best performed by measuring the light emitted in the 430 nm region by the chemiluminescence produced by the reaction of ozone with ethylene. The lowest detection range is 0,05 p.p.m. by volume. For the continuous photometric detection of ozone in a mixed reagent containing iodide and bromide, the following method is often proposed:

0,5 M KBr, 0,001 M KI, 0,01 M KH_2PO_4 and 0,01 M K_2HPO_4.

The detection limit for O_3 is 0,05 p.p.m. by volume. These analysers are also suitable for gaseous ClO_2.

For the continuous measurement of residual ozone in water a direct and specific amperometric detector with a sensitivity of 0,02 g/m^3 has been developed (Masschelein et al. 1977; 1979b). The system is based on the self polarising electrode couple Ni/Ag, AgCl. After preconditioning of the electrodes, the depolarisation current is established as given in Figure 8. The method does not suffer from the interference of active chlorine compounds.
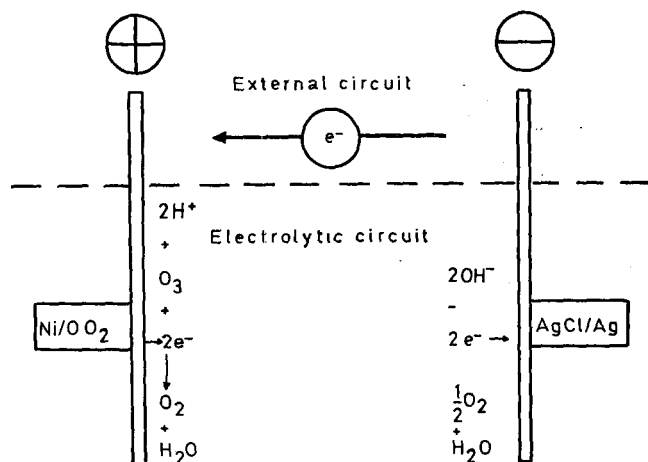
Specific monitoring of residual ClO_2 in water with the possible presence of chlorine and oxychlorine compounds is carried out by the automation of the spectrophotometric method with ACVK. However, for applications on site, a less specific electrochemical technique has been developed (Masschelein and Fransolet, 1979). Similar to the preceding method for ozone, it is based on a galvanic cell constructed with Au and Ag electrodes (See Figure 9). On the addition of iodide to the water at a pH between 4,5 — 5, obtained by the addition of acetic acid, the latter forms an AgI reference electrode.
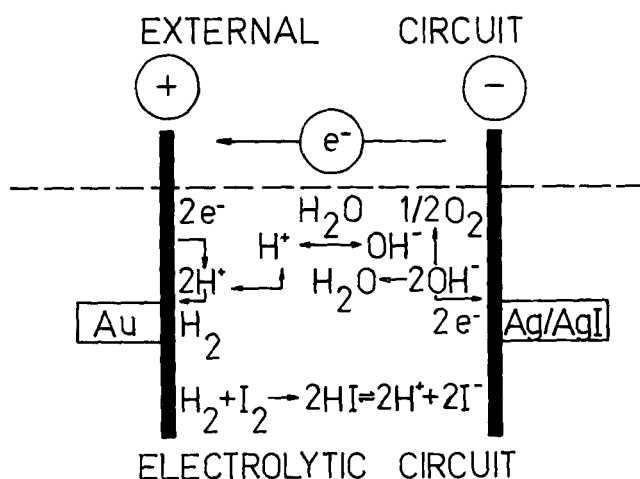

Figure 9
Galvanic cell for the measurement of residual active oxidants (RAO)

The method detects all the oxidants present capable of converting iodide to iodine within approximately 2 min at pH 4,5 to 5. Residual chlorite does not interfere significantly. The detection limit in continuous operation is 0,01 g/m^3 either for chlorine or chlorine dioxide.

Maintenance of the Bacterial Quality of the Water

Ozonised water contains a number of oxidised substances and in particular carboxylic acids which are likely to form a coenzyme, they are, therefore, metabolisable by bacteria. Post-infection causing bacterial aftergrowth is a potential hazard to the quality during the transport and distribution of ozonised water. Its mixing with groundwater can involve a particular case of post-infection. Over 156 different waters from sources ranging from a simple well capacity to the Tailfer plant with a final production capacity of 260 000 m^3/d are currently mixed at the CIBE. Consequently the problem of post-disinfection and potential aftergrowth has been the subject of thorough study and care.

Usual enterobacteria such as coliforms, enterococci, salmonella, etc. do not develop and scarcely survive in water. The problems related to aftergrowth are more often connected with ubiquitous bacteria and organisms causing oxygen depletion, taste and odour. They are sometimes associated with anaerobic
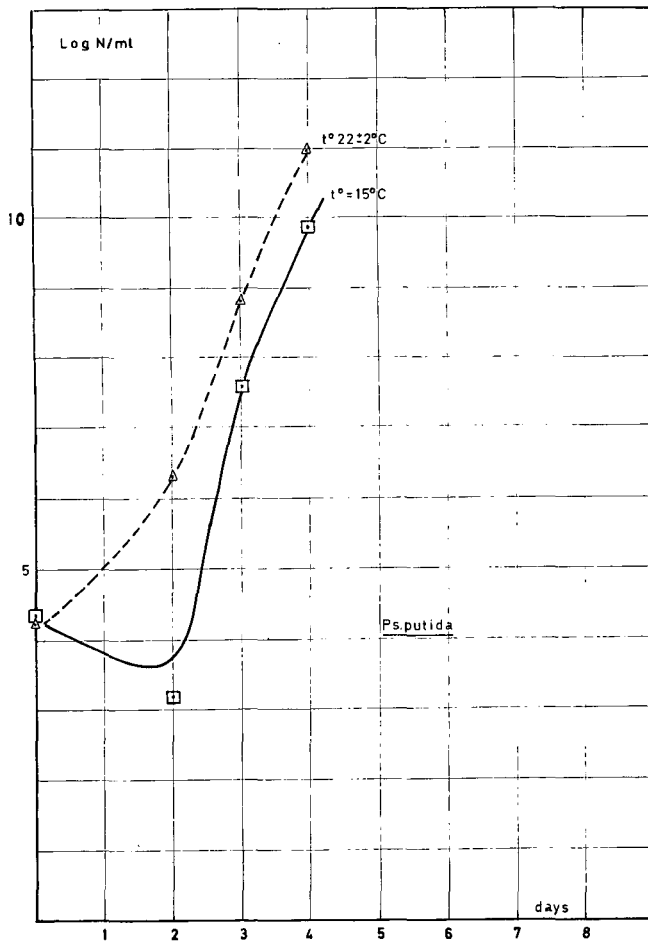

Figure 8
Galvanic cell for the measurement of residual ozone in water

Figure 10
Development of Pseudomonas putida *in ozonised water*

conditions or development of higher organisms such as Asellus and worms. Although it does not constitute a direct sanitary risk it is important to recognise the aftergrowth process in its very early stages and take appropriate preventive measures immediately. Among the bacteria also ubiquitous in groundwater the *Pseudomonas fluorescens* type is the genus that apparently develops the fastest in practical conditions of water distribution. Besides the wild strains well characterised types have also been investigated, e.g. *Pseudomonas putida*, *Pseudomonas deva* and *Pseudomonas cruciviae*, among which *Pseudomonas putida* develops the fastest (Masschelein and Fransolet, 1980).

In Figure 10 the development of *Pseudomonas putida* in ozonised water is given.

Yeasts are often more resistant to disinfection than bacteria and the *Rodotorula* type *(Glutinis* or *Rubra)* is often associated with *Pseudomonacea* in ozonised water.

The principles of the post-disinfection applied at the CIBE

Disinfection with chlorine is practised at the catchment site of groundwaters (gaseous chlorine being progressively replaced by sodium hypochlorite for safety reasons), and post-ammoniation for one minute. The weight ratio $Cl_2:NH_3$ is between 3 and 4. This technique is entirely satisfactory to kill occasional enterobacteria in groundwater ($10-12°C$) and to maintain a residual dose of chloramines right from the catchment point to the service reservoirs. The doses of active chlorine necessary vary between $0,15$ and $0,25$ g/m^3, depending on the distance the water is to be transported.

The water treated at the Tailfer station is pumped to the reservoir of Bois-de-Villers 7 km away, and disinfected in a similar way. However, owing to the changes in temperature of the treated surface water, the doses of chlorine necessary to maintain a sufficient residual concentration during a 60 km transport, are subject to large seasonal variations. The variation in chlorine dosing with temperature is given in Figure 11.
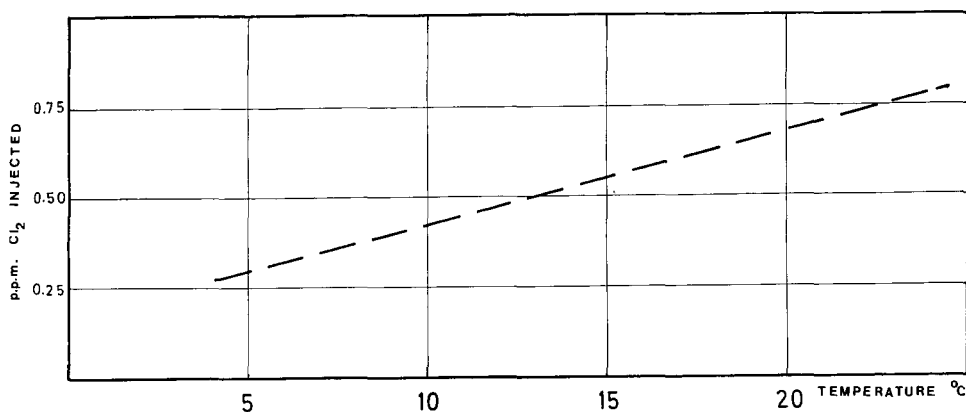

Figure 11
Variation in chlorine dosing with temperature

Water from catchments of low flow may, if necessary, for local distribution, be disinfected with chlorine alone. When mixing into the aqueducts with the main flow these minor amounts of chlorine are stabilized for further transportation by equilibration with the pre-existing monochloramines.

Upon mixing of treated surface water with groundwater of different temperatures there is an increase in chlorine consumption. Therefore a supplementary post-disinfection is put into operation at the entrance of the service reservoirs. During this operation the use of an additional amount of chlorine must often be avoided so as not to form noxious nitrogen trichloride or "overconsume" the chlorine by a "break-point" chlorination of the pre-existing chloramines. Therefore chlorine dioxide is used for post-disinfection at the entrance of the service reservoirs.

Chlorine dioxide used in clear water in controlled conditions has proven to be stable for 48 — 120 h even in trace concentrations. However its stability in water distribution equipment is often way below. Nevertheless, a persistant bacteriostatic and bactericidal activity is maintained. A very significant part of chlorine dioxide is reduced into chlorite. Hence two fundamental questions arise: the first related to the possible toxicity of chlorite and the second to its disinfecting power and bacteriostatic properties.

Residual effects of disinfectants

The residual concentration of chlorine dioxide which does not alter the taste and odour disagreeably in drinking water ranges between 0,4 and 0,5 g/m^3. This dose is also below the acceptable limit when considering the toxicity as tested on rats which gave no indication of any objectionable effect of serological toxicity even at doses up to 5 g/m^3 (Fridlyand and Kagan, 1971). In Belgium, the maximum acceptable residual concentration for drinking water distributed through a public system is 0,25 g/m^3.

' Chlorite is toxic and can cause methaemoglobinaemia. However, the LD_{50} for rats is 140 mg/kg. In the extreme assumption that all of the dioxide could be transformed to chlorite, this LD_{50} dose corresponds to 105 mg/kg of ClO_2. Hence there appears to be no pertinent objection to the use of chlorine dioxide at the usual dose.

The bacterial concept developed at the CIBE is based on a rapid disinfection with chlorine dioxide and a maintenance action with chlorite. Consequently, the limiting effect of residual chlorite is one of the special topics of post-disinfection.

Practical bactericidal and bacteriostatic effect of chlorite

In laboratory research, cultures of a wild strain of *Bacillus enterococcus* were exposed for several days to low concentrations of chlorite. The experiments were executed in agitated physiological water. In these experimental conditions the natural decay, without any chlorite introduced, followed CHICK's law:

$$\log \frac{N}{N_o} = k_{10} t$$

Constants for the enterococcus are: $k_{10} = -0,013$ d^{-1}

In the presence of chlorite, stable in the experimental conditions, the decay was significantly accelerated but an important lethal lag was observed, thus a discrepancy to CHICK's law. The multi-site killing theory enables an interpretation of the results on a relative basis (Masschelein and Debacker, 1980).

A certain number of vital sites must be attained and each at least once, to kill or deactivate the organism completely.

If first order kinetics for each site are accepted then the probability of deactivating m sites is:

$$Pm = (1 - e^{-kt})^m = \frac{N_o - N}{N_o} \quad \text{(that is the fraction of organism killed)}$$

$$\frac{N}{N_0} = 1 - Pm = 1 - (1 - e^{-kt})^m$$

Binomial expansion gives:

$$Pm = (1 - e^{-kt})^m = 1 - me^{-kt} + \frac{m(m-1)}{2} e^{-(kt)2}$$

$$\simeq 1 - me^{-kt}$$

and

$$1 - Pm = \frac{N}{N_o} = m e^{-kt}, \text{ hence}$$

$$\log_{10} \frac{N}{N_0} \simeq \log m - 0,43 k_{10} t$$

The results of this analysis are given in Figure 12.

The bactericidal action of chlorite on enterobacteria appears to be too slow to be an operational method of disinfection. However no development was observed when chlorite is present.

The same method applied to *Pseudomonas putida* (NCIB 8685) also indicates a lethal lag with m numbers of 6 to 8 and bactericidal decay within two to three days for concentrations of ClO_2^- below 1 g/m^3. See Figure 13 for action of chlorite on *Pseudomonas putida*.

In experiments similar to those reported here but with wild strains of *Pseudomonas fluorescens*, a faster killing rate, together with the survival of resistant bacteria were often observed. The colonies present a pinkish colour on the Kings' medium for *Pseudomonas fluorescens*. Organisms of the chromobacter type were suspected but they turned out to be yeasts of the *Rodotorula* type *rubra* or/and *glutinis* (Masschelein, 1978).

Use of other bactericidal residuals

Part of the multisite killing might only be speculative as far as the interpretation of the m number is concerned : m germs living in clusters or m vital centres per germ or a combination of both concepts is always possible besides the fact that the extrapolation to zero time can be subject to errors. Therefore, and also for practical reasons, other weak disinfectants have been examined : monochloramine and hydrogen peroxide. See Figure 14 for mortality of *Pseudomonas putida*.

It appears from these data that germs of the *Pseudomonas* genus probably survive in groups in the water.

Advantages of the Treatment with Chlorine Dioxide and Ozone

The action of chlorine dioxide is at least as bactericidal as that of chlorine (Masschelein, 1979a) and is generally more efficient owing to its higher diffusibility as a radical than is chlorine in an ionised form. Particularly in slightly alkaline medium the
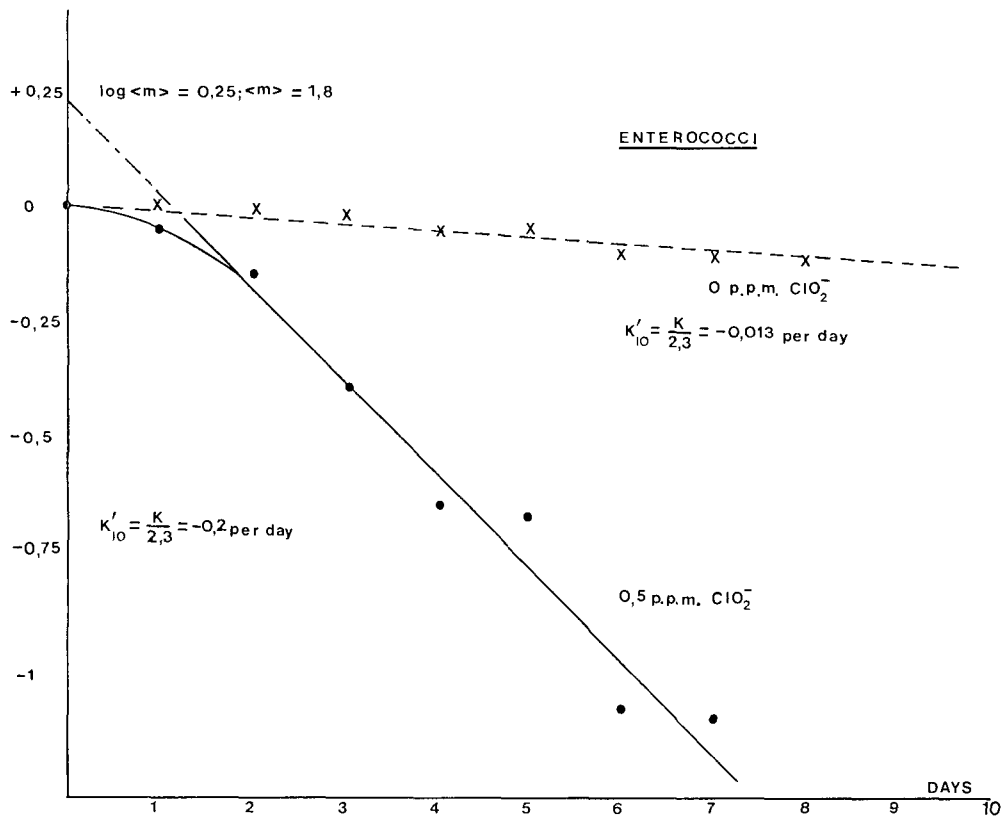
Figure 12

$\log \langle m \rangle = 0{,}25 ; \langle m \rangle = 1{,}8$

$+0{,}25$

ENTEROCOCCI

0

$-0{,}25$

O p.p.m. ClO_2^-

$K'_{10} = \dfrac{K}{2{,}3} = -0{,}013$ per day

$-0{,}5$

$K'_{10} = \dfrac{K}{2{,}3} = -0{,}2$ per day

$-0{,}75$

$0{,}5$ p.p.m. ClO_2^-

-1

DAYS

1 2 3 4 5 6 7 8 9 10

Figure 12
Action of chlorite on enterococci

Figure 13

PUTIDA-Chlorite

$\log \langle m \rangle = 0{,}8 \text{---} m = 6{,}3 = \langle 6 \rangle$

$k_1 C_1^n = k_2 C_2^n \qquad n = 0{,}3$

$0{,}00$

$-0{,}50$

$0{,}2 g/m^3$

-1

$\log(N/N_0)$

$K'_{10} = \dfrac{k}{2{,}3} = 0{,}04 \, h^{-1}$

$1 g/m^3$

$-1{,}5$

-2

$K'_{10} = \dfrac{k}{2{,}3} = 0{,}066 \, h^{-1}$

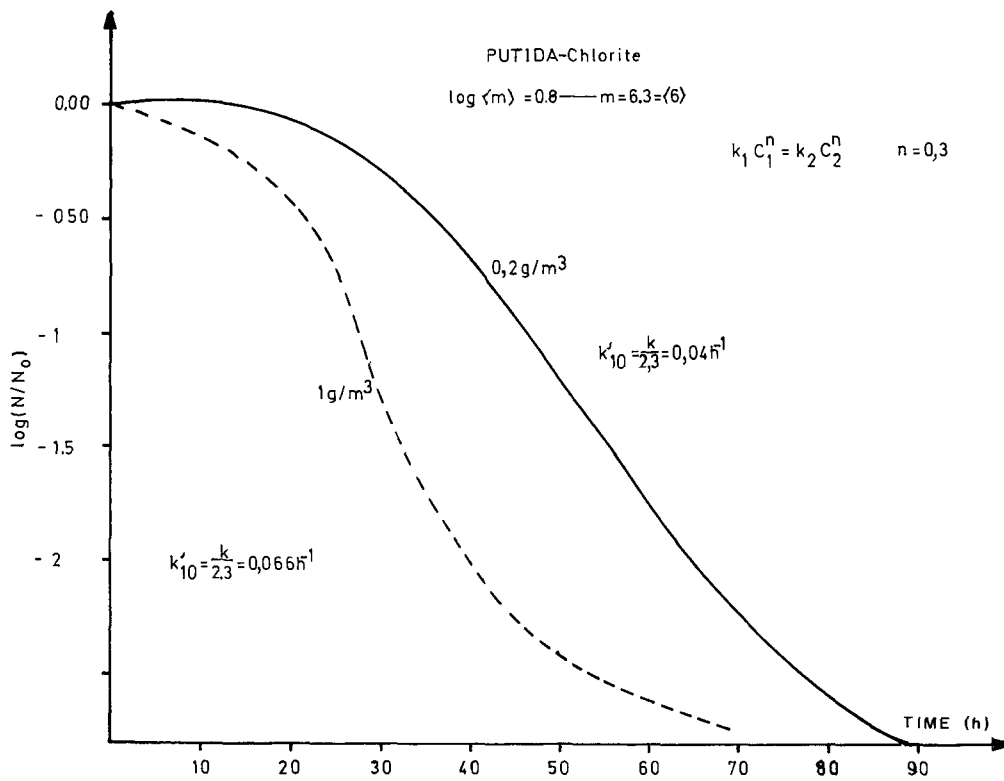TIME (h)

10 20 30 40 50 60 70 80 90

Figure 13
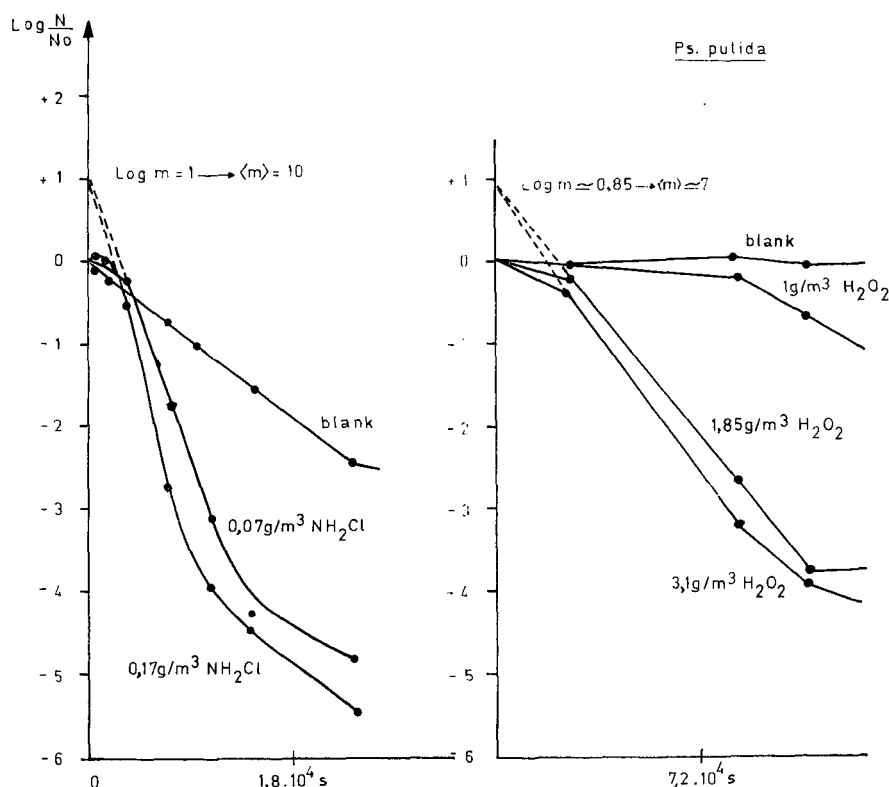*Action of chlorite on Pseudomonas putida*
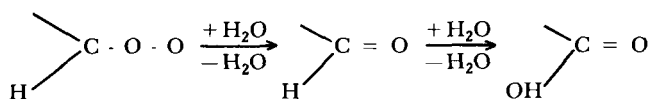
Figure 14
Mortality of Pseudomonas putida

reagent is a faster disinfectant than chlorine. Ozone is well known to be a very strong disinfectant in water treatment. Enterobacteria are killed even at low doses within a few seconds. The viricidal action of ozone is also well known, it is however beyond the scope of this presentation to deal with this aspect in detail. For further information see Masschelein 1969, 1975, 1979a.

The bactericidal efficiency of both chlorine dioxide and ozone (except in alkaline water) is not inhibited by ammonium. In the case of chlorine dioxide especially this is an important property because in pretreatment it is not necessary to exhaust the demand of ammonium compounds as is necessary for chlorine. The proper use of chlorine dioxide on raw water to achieve a disinfection in pretreatment, is to maintain a residual concentration of 0,2 g/m³ for at least 40 min and preferably 1 h. After this treatment no trihalomethanes are formed and the precursors are largely destroyed enabling a much less objectionable post-chlorination.

Moreover, chlorine dioxide is only slowly decomposed by activated carbon thus enabling the maintenance of bactericidal action in the sludge layer of a settling tank when powdered carbon is used in the coagulation phase. Chlorine dioxide and especially ozone alter or destroy the protecting hydrophilic agglomeration on colloids and can thus promote the coagulation phase. In this action just like in disinfection, rapid mixing with water recirculation is essential.

It is beyond the scope of this paper to detail the reactivity of chlorine dioxide and ozone with dissolved products. However, a few aspects should be mentioned:

● Bromide is partially oxidised by chlorine dioxide as well as by ozone to yield bromine;

● Contrary to ozone, chlorine dioxide reacts rapidly with aldehydes and releases the corresponding carboxylic acids;

● Chlorine dioxide does not directly chlorinate organic compounds, however, in some instances (Masschelein, 1979a) besides direct oxidation, the addition of a OClO radical may occur at a double bond. The adduct can disproportionate to an alpha-chloroketonic function. The formation of chlorinated products by this mechanism is always in competition with that of oxidised molecules by the substitution by an OClO radical at a position adjacent, to a double bond followed by a dehalogenation. On the other hand, in water ozone forms practically only peroxy bonds instead of ozonides obtained in less polar solvents, but carbonyl groups (either aldehydic or carboxylic) are formed through transposing.

$$\overset{\diagdown}{\underset{H\diagup}{}}C \cdot O \cdot O \xrightarrow[-H_2O]{+H_2O} \overset{\diagdown}{\underset{H\diagup}{}}C = O \xrightarrow[-H_2O]{+H_2O} \overset{\diagdown}{\underset{OH\diagup}{}}C = O$$

Both of these chemicals release more oxygenated oxidised derivatives than by means of possible biodegradation. The action of ozone on dissolved refractory substances or viruses requires several minutes. Therefore a contact time for sufficient action of a residual concentration is essential.

Conclusions

Chlorine dioxide and ozone are both oxidising gases that must be generated on the site of application. The synthesis of chlorine dioxide from chlorite gives high yields. The generation of ozone is, however, a low yield process, from the thermodynamic point of view, and progress in the technology of the design of ozonators is still required.

Treatment of water with chlorine dioxide is a simple mixing process but with ozone it needs considerable skill. This requires a concentrated ozone bubble contact system and particularly in post-ozonation a contact time for residual dissolved ozone is necessary. Both gases are toxic and appropriate ventilation of a work-room is necessary and in the case of ozone, destruction of the off-gases is an inherent part of the design.

Both oxidants, if properly used, limit or even prevent the formation of trihalomethanes. In the use of chlorine dioxide a stable bacteriostatic effect remains in the water. In ozonised water a high risk of bacterial aftergrowth is present. Therefore appropriate post-disinfection techniques must be provided by the combination of chlorination, post-ammoniation and the use of chlorine dioxide and U.V. light as an alternative.

Treatment by both chlorine dioxide and ozone results in a greater number of biologically degradable compounds, than does treatment by chlorine. A proper design of treatment plants will limit excessive use of chlorine and the resulting formation of chlorinated products. There is a need for further investigations into the sequence of treatment processes.

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