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APPLICATION OF CHLORINE DIOXIDE IN INFILTRATION WATER TREATMENT

Chlorine dioxide demand was determined in infiltration water after its treatment by aeration, aeration + sand filtration or by aeration + sand filtration + GAC sorption. The effect of TOC concentration on the chlorine dioxide dose was examined in more detail. It was found that the oxidizing activity of the chlorine dioxide in the water accounted for the formation of some oxidation by-products. The study also showed that chlorine dioxide not only acted as a disinfectant but also contributed to the reduction of coloured matter and TOC in the water treated. As it can be inferred from the analysis of the results obtained, the dose necessary to meet the chlorine dioxide demand in infiltration water depended heavily on the initial TOC concentration.

1. INTRODUCTION

Chlorine dioxide interacts with bacterial and viral biomolecules, thus impairing the physiological functions of the cells. It can damage the internal cell membrane and permit the access of the disinfectant to the interior of cysts and spores. Chlorine oxide is also capable of producing disturbances during replication of viral RNA. It easily reacts with amino acids (proline, hydroxyproline, histidine, cystine, cysteine or tyrosine) and fatty acids. To attain an effective deactivation of protozoan cysts and algae, a notably higher cT product than the one normally used for water disinfection is needed.

Chlorine dioxide affects noticeably bacteriophages, viruses (e.g. *polio*), or protozoan cysts (*Cryptosporidium parvum*, *Naegleria fowleri* or *Giardia muris*), which are immune to the action of chlorine. The concentration of residual chlorine dioxide approaching 1.0 g ClO₂/m³ suffices to deactivate *Eberthella typhosa*, *Shigella dysenteriae*, *Salmonella typhosa* and *Salmonella paratyphi* cells in the water under treatment. A slightly higher concentration of residual chlorine dioxide protects the water users against *Pseudomonas aeruginosa* and *Staphylococcus aureus*. But this disinfectant is less effective than ozone in killing the *Giardia* cysts, although, compared to ozone, its stability and bactericidal activity are of a longer duration in the water-pipe network, spe-

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cifically with respect to the *Aeromonas* which is known for its ease to colonize pipelines. Chlorine dioxide is an efficient destroyer of *Clostridium perfringens*, a bacterial species with particular resistance to the action of chlorine. Unlike chlorine, chlorine dioxide does not prevent the formation of a biofilm on the pipe walls, but the biological film of the encrustation contains a greater number of surviving bacteria when exposed to chlorine dioxide than when exposed to chlorine. Of particular importance is the bactericidal effect of chlorine dioxide on the *Legionella* genus, which is often detected in the biofilm but very resistant to chlorination. When use is made of chlorine dioxide in the pre-oxidation process, the benefits can be itemized as follows: destruction of algae of the *Scenedesmus*, *Monoraphidium*, *Chlorella*, *Chlamydomonas* and *Cyanobacteria* genera and reduction of the unpleasant taste and smell produced as a result of algal metabolism. Chlorine dioxide doses high enough to destroy algae vary from 0.3 to 1.0 g ClO₂/m³. The efficiency of chlorine dioxide is higher than that of chlorine [1].

2. TECHNOLOGICAL ASPECTS OF CHLORINE DIOXIDE IN WATER TREATMENT

Chlorine dioxide has long been used with success as disinfectant in water treatment trains in many different countries. Owing to its high oxidizing potential and a remarkable stability in aqueous environment as well as the lack of propensity to generate organic halogen derivatives, many waterworks have substituted chlorine dioxide for the previously used chlorine. The application of chlorine dioxide has become particularly popular in Belgium, Germany, France, Italy, Sweden and Switzerland. In the USA, nearly 500 water treatment plants make use of this disinfectant. Normally, water disinfection with chlorine dioxide yields a high deactivation of viruses and bacteria, and the disinfectant itself is characterized by a high stability in the water-pipe network.

Advances in the technology of water disinfection with chlorine dioxide were induced by the researchers' reports on the detrimental effect the products of which are formed when chlorine (used as disinfectant) reacts with organic compounds present in the water. Compared to chlorination, an obvious advantage of the chlorine dioxide disinfection method lies in the fact that no trihalomethanes (THM) form in the reaction of pure chlorine dioxide with humic and fulvic acids. Exposed to chlorine dioxide, the compounds with unsaturated bonds in their structure are easily oxidized. Another major advantage of chlorine dioxide over chlorine is its ability to oxidize completely the phenols that are present in the water; chlorine added to phenols-containing water accounts for the formation of chlorophenols and the release of unpleasant smell. If the water under treatment contains phenol compounds in the form of phenol ions, they will be oxidized immediately by chlorine dioxide; non-dissociated phenols react with chlorine dioxide at a very slow rate. Chlorine dioxide in excess supports the formation of *p*-benzoquinone (45%) as well as maleic and oxalic acids. However, if phenols are

in excess, they are responsible for formation of chlorophenols. Typically, chlorine dioxide is non-reactive in the presence of aromatic hydrocarbons and aliphatic olefins.

Yet, the use of chlorine dioxide is known to have some adverse side effects. These are the by-products of its reaction with the waterborne organic matter which generates oxyderivative compounds in the water, i.e. chlorites and chlorates, as well as carbonyl compounds, i.e. formaldehyde, acetaldehyde, glyoxal and methylglyoxal. However, the concentrations of these compounds in the water being treated have not been reported harmful. It has been found that the mutagenic activity of the water induced by the application of chlorine dioxide is lower than that resulting from the use of chlorine or chloramines as a disinfectant.

In Poland, the application of chlorine dioxide dates back to 1992 (when several water treatment plants decided to use this reagent for water disinfection) and has become an increasingly frequent practice since then. The first attempts to replace chlorine with chlorine dioxide were made in the late 1950s. Thus, in 1958, the Waterworks Pomorzany, Szczecin, started using chlorine dioxide to upgrade the organoleptic properties of the water. In 1962, the chemical plant ROKITA, Brzeg Dolny, Lower Silesia, disinfected water with chlorine dioxide [2]. These days the interest in the use of chlorine dioxide continues to increase in Poland, thus stimulating research on the disinfectant demand for water treatment. Consideration is given to the correlation between the water quality and the chlorine dioxide demand in water, which will enable a quick assessment of the dosage required [3], [4].

A major toxic effect linked with water disinfection involving chlorine dioxide is that of the products of the disproportionation reaction. Chlorites and chlorates have been found to produce hemolytic anemia due to the oxidation of erythrocyte cell membranes. At increased concentrations, chlorites induce methemoglobinemia. Chlorine dioxide does not affect blood cells, though it reduces the levels of tyrosine (a thyroid hormone) due to the interaction with iodides. Being a strong oxidizer, chlorine dioxide accounts for their oxidation and consequently their reaction with organic compounds. When humans suffering from the deficiency of glucosi-6-phosphate dehydrogenase are exposed to chlorine dioxide, chlorites or chlorates in the dose of 0.036 mg/kg d, this is concomitant with undesirable changes in their serum and blood. No health implications as a result of exposure to chlorine dioxide and disproportionation reaction products (which occur in water disinfected with doses normally used in treatment technology) have been reported so far. The regulations specifying the admissible concentrations of chlorites and chlorates are not very clearly defined, and so only few countries have issued relevant standards. The WHO recommends that the concentration of chlorites should not exceed $0.2 \text{ g ClO}_2^-/\text{m}^3$. The US Environmental Protection Agency allows a total concentration of residual ClO_2^- , ClO_3^- and ClO_2 as high as $1.0 \text{ g}/\text{m}^3$, but this is because in the United States of America chlorine dioxide is widely used for water disinfection. In Germany (where chlorine dioxide is used for final disinfection, compulsorily carried out for as much as 70% of the water volume

treated for drinking purposes), the admissible chlorine dioxide dose, the maximal residual chlorine dioxide concentration, and the maximal chlorite concentration amount to 0.4 g ClO_2/m^3 , 0.2 g ClO_2/m^3 , and 0.2 g $\text{ClO}_2^-/\text{m}^3$, respectively. In Belgium and Switzerland, the allowable concentration of chlorites in potable water is up to 0.25 g $\text{ClO}_2^-/\text{m}^3$ and up to 0.15 g $\text{ClO}_2^-/\text{m}^3$, respectively [5].

In Poland, the Ministry of Health and Social Welfare as well as the National Institute of Hygiene have officially supported and accepted the implementation of chlorine dioxide in water treatment for drinking purposes since 1992, but no detailed regulations or admissible concentrations have been published so far. In the decree of 19 November, 2002 (Government Regulations and Laws Gazette No. 203 par. 1718), the Ministry of Health specified the admissible concentrations of chlorine dioxide in the by-products of potable water disinfection with this compound as follows: chlorates, 0.2 g $\text{ClO}_3^-/\text{m}^3$ and chlorites 0.2 g $\text{ClO}_2^-/\text{m}^3$. These values imply indirectly that the chlorine dioxide dose practically must not exceed 0.4 g ClO_2/m^3 , which is difficult to achieve in many waterworks involving surface water and infiltrated water intakes.

It should be emphasized that chlorine dioxide neither provokes nor promotes mutagenic effects. However, the products of chlorine dioxide reactions with other compounds may act as carcinogens. Experiments on animals have substantiated the carcinogenic effects exerted by acetaldehyde and formaldehyde, which are formed in the reaction of chlorine dioxide with quaternary amines and amino acids. The yield of aldehydes in water disinfected with chlorine dioxide is comparable with that in ozonated water. Quinones and benzoquinones (which owe their origin to the presence of aromatics and phenols) have also been found to act as carcinogens. But chlorine dioxide has another major advantage: the ability to oxidize inorganic compounds (e.g. sulphides, manganese(II) compounds and iron(II) compounds) without reacting with ammonia nitrogen which is present in the water. Thus, the use of chlorine dioxide for the treatment of ammonium ion-containing water does not raise its demand for this disinfectant – contrary to what can be observed when chlorine is used for water disinfection. Moreover, the products of the reaction of chlorine dioxide with the pollutants present in the water are neutral substances in terms of taste and smell. If nitrite nitrogen is present in the water to be treated, chlorine dioxide will oxidize it to nitrate nitrogen, though with the formation of chlorites. Chlorine dioxide is also able to oxidize iodides and cyanates; the latter only in an alkaline medium.

Similar reactions with inorganic compounds are also typical of ozone. However, the advantage of chlorine dioxide over ozone lies in the higher stability of the former in an aqueous medium, and this is what justifies the application of chlorine dioxide as a final disinfectant before sending the water to the pipe network. Another benefit of using chlorine dioxide for this purpose is that this disinfectant does not react with bromides, thus preventing the formation of bromic THM derivatives.

3. MATERIALS AND METHODS

To determine the chlorine dioxide demand in water, laboratory tests were run with infiltration water and the following treatment trains [6]–[9]:

- Aeration.
- Aeration + pH adjustment with lime + rapid filtration.
- Aeration + pH adjustment with lime + rapid filtration + adsorption on activated carbon.

The infiltration water used in the tests was subject to aeration in a multiple-tray aerator (at a load approaching $60 \text{ m}^3/\text{m}^2\text{h}$) and rapid filtration through ripened sand beds (at a rate of about 6 m/h). Upon aeration (prior to filtration), pH was adjusted with lime water. Adsorption on activated carbon and oxidation with chlorine dioxide were performed in a batch system, using granular activated carbon (GAC) ($25 \text{ g}/\text{m}^3$) and chlorine dioxide obtained under laboratory conditions (doses, up to $3.0 \text{ g ClO}_2/\text{m}^3$; contact time, 30 min), respectively.

The technological effects achieved with these processes were established based on the variations in the following water quality parameters: turbidity, colour, pH, TOC, residual chlorine dioxide concentration, and chlorite concentration. The samples of water being treated were subject to microbiological analysis. The water quality parameters of interest were determined using relevant standard methods (TOC with a Shimadzu analyzer; colour by spectrophotometry; turbidity with a Hach analyzer; chlorine dioxide and chlorite concentrations with the modified Aieta method).

4. RESULTS AND DISCUSSION

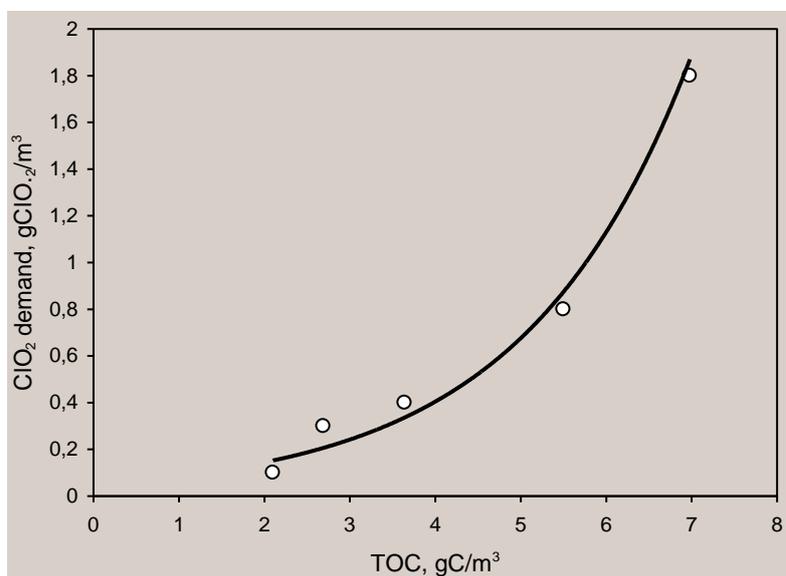
Table 1 shows the variations in some of the water quality parameters during its oxidation with chlorine dioxide.

Table 1

Characterization of infiltration water

Parameter	Aerated water	Water filtered through sand	Water filtered through sand + GAC
Turbidity, NTU	12–17	0.4–0.9	0.4–0.7
Colour, g Pt/m ³	10–15	7–10	3–4
pH	7.5–7.6	7.6–7.8	6.2–7.4
COD, g O ₂ /m ³	2.5	2.0–2.5	0.9–1.0
TOC, g C/m ³	3.7–7.0	3.6–5.6	2.1–2.7
Total iron, g Fe/m ³	0.3	<0.2	<0.2
Manganese, g Mn/m ³	0.5–0.6	<0.05	<0.05

The infiltration water under test displayed increased turbidity, slightly elevated concentrations of iron compounds and increased levels of manganese compounds. Organic matter content expressed as COD was low while that expressed as TOC was temporarily increased. The chlorine dioxide demand in water was determined using the criterion of residual chlorine dioxide concentration in the water, which varied between 0.05 and 0.25 g ClO_2/m^3 . It was found that with a TOC content of up to 3 g C/m^3 the chlorine dioxide demand in water did not exceed 0.5 g ClO_2/m^3 (the figure). This relation, however, is not an absolute one; with the same TOC concentration in raw and treated water, the chlorine dioxide demand took different values. And this implies that the chlorine dioxide demand in water cannot be established solely on the basis of the TOC content criterion. In the course of oxidation, a reduction in the content of coloured matter and TOC concentration was observed (table 2).



Chlorine dioxide demand versus TOC content in infiltration water

When the water was treated by means of aeration and filtration, chlorine dioxide demand ranged between 0.4 and 0.8 g ClO_2/m^3 , the residual chlorine dioxide concentration varying from 0.04 to 0.08 g ClO_2/m^3 . Although the addition of chlorine dioxide brought about a reduction in coloured matter content, this was concomitant with a slight increase in turbidity (table 2).

Such an effect is possibly associated with the chemical changes in the organic compounds that occur in the water under the influence of chlorine dioxide, up to a partial mineralization, as it can be inferred from the slight rise in turbidity. This is an indication that better treatment effects and a further TOC reduction appear to be

achievable, which means that the chlorine dioxide demand in water might be reduced, e.g., to the value required for disinfecting purposes. The chlorine dioxide dose for the purpose of disinfection amounted to 0.5 g ClO₂/m³. Chlorine dioxide had a strong bactericidal effect on mesophilic and psychrophilic organisms, and a slightly poorer one on the *coli* group bacteria.

Table 2

Characterization of water after chlorination with ClO₂

Parameter	Aerated water	Water filtered through sand	Water filtered through sand + GAC
ClO ₂ dose, g ClO ₂ /m ³	1.7–1.8	0.4–0.8	0.1–0.3
Chlorine dioxide, g ClO ₂ /m ³	0.08–0.25	0.04–0.08	0.04–0.23
Chlorite, g ClO ₂ ⁻ /m ³	1.48	0.14	0.04
Colour, g Pt/m ³	7–9	7	2–3
Turbidity, NTU	12–17	1.2–1.3	0.6–1.1
TOC, g C/m ³	6.9	3.6	2.1

The inclusion of GAC adsorption in the treatment train reduced the chlorine dioxide demand in water to 0.1–0.3 g ClO₂/m³ at a residual chlorine dioxide concentration ranging between 0.04 and 0.23 g ClO₂/m³. The concentration of chlorites in the water was low. Coloured matter content was found to decrease with increasing chlorine dioxide dose. Turbidity slightly increased, and TOC concentration showed a tendency to remain stable (table 2).

5. CONCLUSIONS

1. In our experimental study, the chlorine dioxide demand in water depended primarily on the TOC concentration and the treatment effect desired. The chlorine dioxide doses necessary for water disinfection were lower than the chlorine dioxide demand in water. The treatment train consisting in pH adjustment and rapid filtration yielded water of a quality which met the demands accepted for potable water, but the chlorine dioxide demand was very high. Upon incorporation of the GAC adsorption process into the treatment train, the demand for chlorine dioxide could be reduced to the values specified in German sanitary regulations.

2. When use is made of chlorine dioxide, this is always concomitant with the formation of chlorites, whose concentration decreases as the concentration of a residual ClO₂ increases. In our study, the use of chlorine dioxide initially brought about a rise in water turbidity but, owing to the high treatment efficiency obtained, this rise was insignificant in terms of the water quality required. The application of chlorine dioxide was also linked with a reduction in coloured matter concentration. The increase in the chlorine

dioxide dose was found to decrease the concentration of TOC. With the treatment train applied, it was possible to reduce the TOC content to about 2.1–2.5 g C/m³.

3. The results obtained have substantiated the furtherance of our research on the modernization of the treatment technology for infiltration water where use is made of chlorine dioxide and a treatment train involving oxidation and adsorption in order to further reduce the concentrations of organic compounds in water and to build up its biological stability in a pipeline.

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ZAPOTRZEBOWANIE WÓD INFILTRACYJNYCH NA DWUTLENEK CHLORU

Określono zapotrzebowanie na dwutlenek chloru wody infiltracyjnej, którą oczyszczono w układach technologicznych obejmujących procesy napowietrzania i filtracji pospiesznej oraz napowietrzania, filtracji pospiesznej i sorpcji na węglu aktywnym. Przeanalizowano wpływ zawartości ogólnego węgla organicznego w wodzie na dawkę dwutlenku chloru. Stwierdzono, że wskutek utleniającego działania dwutlenku chloru w wodzie pojawiają się uboczne produkty utleniania, których zawartość maleje, gdy w wodzie pozostaje wolny dwutlenek chloru. Wykazano także, że stosowanie dwutlenku chloru, poza działaniem dezynfekcyjnym, spowodowało obniżenie intensywności barwy i zawartości substancji organicznych (OWO) w uzdatnianej wodzie. Wykazano, że dawka pokrywająca zapotrzebowanie wody na dwutlenek chloru wyraźnie zależała od początkowej zawartości ogólnego węgla organicznego.