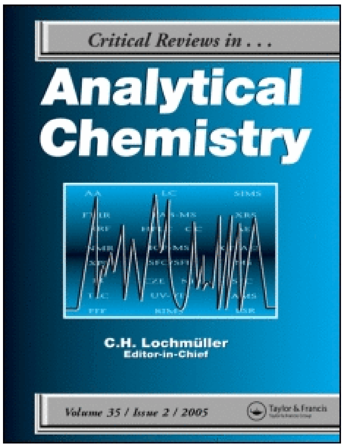

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USING OF OZONE IN HIGH QUALITY DRINKING WATER PRODUCTION

REIN MUNTER, SVEN KAMENEV, JUHA KALLAS,**
LEA MARIPUU*
Tallinn Technical University
*** Institute of Chemistry, Tallinn**
**** Lappeenranta University of Technology, Finland**

Introduction

Interest in the use of ozone for drinking water production has been steadily increasing over the last several years worldwide. In Europe, the EEC regulations on drinking water quality also lead to an increasing interest in ozone use. The discovery of trihalomethanes (THM) as chlorination by-products in 1973 provided the impetus for this particular application [1].

In Estonia, the new Drinking Water Standard EVS 663 was enacted in 1995. According to this standard the drinking water is classified into three quality levels: very good (5), good (4) and satisfactory (3).

Nowadays the drinking water in Tallinn produced from the Lake Ülemiste water corresponds by the majority of its parameters (taste, odor, coliform bacteria, ammonia, nitrates, nitrites, aluminium, total iron, heavy metals etc.) to the drinking water of a good and a very good quality. However, a better reduction of the COD_{Mn} as well as the color and turbidity is needed. The THM (as chloroform) content in drinking water has been less than the Estonian Standard's and WHO's guideline (0.2 g/m^3), but much higher than the EEC guideline (0.04 g/m^3) (**Table 1**) [2].

The water treatment process at the Tallinn Plant (capacity about 170,000 m^3/d) has consisted of raw water **prechlorination, microstraining, coagulation-flocculation, clarification, GAC-sand filtration and postchlorination.** For pretreatment of raw water the prechlorine with dose 4-10 g/m^3 has been used depending on the season. Coagulation and flocculation has been carried out with aluminium sulphate in liquid form (7-8 g/m^3 Al_2O_3) and Magnafloc (0.15-0.2 g/m^3). For disinfection of water before distribution the postchlorine (1.0-1.5 g/m^3) has been used.

Several serious problems in connection with the catchment area and also raw lake water quality parameters (see **Table 1**) have complicated production of drinking water of good and very good quality. The main reasons have been industrial and agricultural pollution during last decades. To prevent infectious diseases and to kill majority of algae cells in raw water, the increased prechlorine doses have been applied for water disinfection, which has produced the corresponding increased concentrations of THM like chloroform.

To produce the drinking water of a very good quality according to the Estonian and EEC standards and to avoid the THM's formation entirely, it was decided to replace the **prechlorination** stage by **preozonation.** In 1992 the TALLINN OZONE PROJECT in cooperation with the french company TRAILIGAZ was started. It will be implemented in 1997.

TABLE 1

Some Raw and Drinking Water Quality Data in 1995 and the Guidelines

Parameter	Unit	Raw water (max.)	Drinking water (max.)	Estonian Standard class (5)	Estonian Standard class (4)	EEC Standard (trend)
COD_{Mn}	g/m^3	17.5	5.6	1.0	2.0	2.0
Color	Pt-Co deg.	60	12	5	15	1.0
Turbidity	g/m^3	10	1.4	0.58	1.16	0.2
Thermotolerant coli	colon./l	1400	0	0	0	0
Phytoplankton	cells/ml	2.5 milj.	0	0	0	0
Zooplankton	$units/m^3$	13.3 milj.	0	0	0	0
Ammonia	g/m^3	0.19	0.15	0	0.5	0.05
Nitrates	g/m^3	5.56	4.15	1.0	10	25
Nitrites	g/m^3	0.028	0.008	0	0.01	0.1
Aluminium	g/m^3	-	0.2	0.2	0.2	0.05
Chloroform	g/m^3	-	0.172	0.2	0.2	0.04

Several very different aspects of Lake Ülemiste raw water ozonation (rate of decoloration with ozone, ozone reaction rate constants with humic substances, impact of turbidity and contact time on the decoloration effect, mass transfer of ozone, optimum contact equipment design, ozonation by-products formation etc.) were previously studied in the laboratory of the Chemical Engineering Department of the Tallinn Technical University as well as under the pilotplant conditions at the Tallinn Plant.

Materials and Methods

Laboratory experiments of ozonation of Lake Ülemiste water were carried out in a semicontinuous bubble column ($V=1.5 \cdot 10^{-3}$ m^3). Ozone-air mixture produced in the laboratory ozone generator (4.5 g/h O_3) was dispersed by the porous plate and led through the bubble column with the gas flow rate in the range of 1-3 l/min. The temperature was kept constant (10, 15, 20 or 25° C). The ozone dose applied was in the range from 0 to 25 g/m^3 of water. Ozone concentration in the gas phase (inlet and outlet) was measured by the ozone analyzer "1003 HC" (Dasibi Environ.Corp., USA) or by the spectrophotometer "SPECORD UV/VIS" at 254 nm. The concentration of dissolved ozone was measured using indigo method [3]. Reactions of ozonation were stopped by adding 1 ml of Na_2SO_3 solution (0.5 mg/ml). The tests were carried out in the neutral, acid and basic media.

In the case of possible contamination of lake water with resistable to molecular ozone pollutants (pesticides etc.) the problem may be solved using highly active ·OH radicals produced in the system H_2O_2/O_3 [4]. Preliminary experiments with Peroxone (H_2O_2/O_3) were carried out with the corresponding ratio of 0.1-0.2 mM/mg.

Ozonation and Peroxone process oxidation by-products were identified by the GC-MS technique - Hewlett-Packard GC 5890 with 5971 series mass selective detector. The samples were extracted by diethyl ether.

For bromate ion possible formation simulation the reaction equations from literature [5] were adapted together with typical to Lake Ülemiste raw water quality data.

Pilot plant tests were carried out at the Tallinn Plant using raw lake water after microscreening with the flow rate of 0.9-3.0 m^3/h. Gas (ozone-air mixture) flow rate was in the range of 0.9-2.0 m^3/h and ozone concentration in the inlet gas 8-23 g/m^3. The ozone dose applied was in the range of 0-24 g/m^3. The pilot plant comprised ozone generator (7-24 g/h O_3), preozonation bubble column ($V=1.2$ m^3), sludge blanket clarifier ($D=0.84$ m; $H=6.0$ m), and a two-layer filter with sand and GAC ($D=0.2$ m; $H=6.0$ m). After reaching the steady-state conditions samples were taken from five points for the color, turbidity, biomass and algae content determination.

Experimental Results and Discussion

Ozone reactions with humic substances and oxidation by-products

The rate of dissolved ozone decomposition in lake water was determined at the temperatures 5-25° C. It was established that ozone concentration reduction in lake water due to its decomposition and chemical reactions with humic matter proceeds according to the 3/2 order with respect to ozone concentration in the liquid phase:

$$dC_{O3}/dt = k_{3/2} \cdot C_{O3}^{3/2} \qquad (1)$$

Depending on the lake water pH and chemical composition (specific conductivity χ) the following values for $k_{3/2}$ were established (Table 2):

TABLE 2

Average Values of the Decomposition Rate Constant $k_{3/2}$ at 15° C

Water	pH	χ, $cm^{-1} \cdot m^{-1}$	$k_{3/2}$, $M^{-0.5} \cdot s^{-1}$	Correlation coefficient
Lake water	7.1	$4.7 \cdot 10^{-2}$	0.211	0.980
Lake water + Na_2CO_3	8.4	$3.4 \cdot 10^{-2}$	0.537	0.999
Lake water + H_2SO_4	4.6	-	0.197	0.990

The data in **Table 2** indicate that with increasing of pH from 7.1 to 8.4 the overall decomposition rate of ozone increases about 2.6 times. The decomposition rate of ozone in distilled water was determined separately. The average value of the $k_{3/2}$ at 15° C was 0.0038 $M^{-0.5} \cdot s^{-1}$.

Using the composed mathematical model of the semicontinuous bubble column [6] and the values of ozone degradation rate constants in distilled water and in the lake water at the same pH and temperature, the degradation curves of ozone due to pure chemical reaction with humic and fulvic acids in lake water were calculated. The values of the corresponding rate constant of second order k_2 are given in **Table 3.**

TABLE 3

Reaction rate constants of ozone with humic and fulvic acids in lake water

pH	k_2, $M^{-1} \cdot s^{-1}$	Correlation coefficient
4.8	18.6	0.942
7.0	22.2	0.955
8.5	33.3	0.926

Comparison of the dissolved ozone degradation overall rate constants in lake water (**Table 2**) with the pure chemical reaction rate constants of ozone with humic and fulvic acids (**Table 3**) indicated that with increasing of pH from neutral to basic media the overall velocity of ozone decomposition increases about 3 times, while the direct oxidation reactions are accelerated only about 1.5 times. It means that ozonation of raw lake water should be carried out at as lower pH as possible, and that **the humic and fulvic acids in lake water are oxidized mainly with molecular ozone.**

As the by-products of oxidation with ozone and H_2O_2/O_3 unexpectedly quite complicated by-products like 1-ethoxy butane, 1-methylethylbenzene, limonene,
2-ethyl-1,3-dimethylbenzene, octadecane, heptadecane, tetratetracontane, tetratriacontane, hexacosane, hexatriacontane etc. were identified instead of conventional simple aldehydes, ketones and carboxcylic acids. It may be due to too low dose of applied ozone (4 g/m^3) on one hand, or due to the extragent (diethyl ether) used on another.

A special attention among the ozonation by-products formation was paid to the bromide-bromate issue (the EEC guideline for bromate in drinking water is
0.025 g/m^3). Analyses of the Lake Ülemiste raw water indicated the bromide ion content in the range of 0.01-0.03 g/m^3. Using the chemical equations involved in bromate formation [5] and the raw lake water average quality data:
$[NH_4^+]=0\text{-}0.2$ g/m^3; $[HCO_3^-]=168$ g/m^3; the reactions of bromate formation were simulated at the dose of injected ozone 4 g/m^3. It was proved that only in the case when ammonia content in raw water is zero, about 0.045 g/m^3 of bromate ion can be formed in drinking water. At average ammonia content (0.1 g/m^3) the amount of bromate formed is already zero and no real danger of toxic bromate formation at the Tallinn Plant exists when implementing preozonation.

The main results of the pilot plant tests

Measurements of the raw lake water color reduction with ozone at different values of pH confirmed the theoretical conclusions given above. The color reduction (in %) was significantly diminished when ozonation was carried out at higher values of pH
(>7.0). The curves of the color reduction of lake water can be divided into two stages: fast oxidation of humic acids and slow oxidation of more resistable fulvic acids.

The dose of applied ozone 4-6 g/m^3 reduces the color of raw water at the first stage of ozonation approximately by 15 degrees at the values of initial color 35-55 degrees.

At the first stage the color reduction depends only on the ozone dose consumed and not on the contact time, which was varied during laboratory and pilot plant tests in the range of 3-4 to 480 s using different contact equipment. Calculation of the ozone chemosorption parameters in raw lake water according to Danckwerts [7] indicated that the chemical reaction rate enhancement factor κ was in the range of 2.9-3.3 [8], which means that the raw water decoloration with ozone proceeds in the regime of the fast chemical reaction and the whole process is controlled by the ozone mass transfer, especially by the value of the interfacial area.

The aim of the **preozonation** is to reduce the color at the first stage, to kill the algae cells and to inactivate the microorganisms and viruses in raw water. To reach the 99.9% of lake water disinfection by *Escherichia Coli* the dose of applied ozone at least of 2.5 g/m^3 is needed.

During the pilot plant tests the efficiency of **preozone** and **prechlorine** for color, turbidity and biomass reduction in raw lake water was tested. Different doses of alum coagulant (11-20 g/m^3 Al_2O_3) with flocculant (0.2-0.4 g/m^3 PAA) were added to the prechlorinated and preozonated water (6-7 g/m^3 of applied oxidant). The results are presented in **Table 4.**

TABLE 4

Comparative efficiency of preozone and prechlorine

O_3, g/m^3	Cl_2,g/m^3	Color, deg.	Reduction, %	Turbidity, g/m^3	Reduction, %	Biomass g/m^3	Reduction, %
8.0		7.0	81.6	1.6	90.6	0.11	99.7
	6.0	12.0	68.4	7.1	58.2	8.58	72.3
7.0		10.0	77.3	3.0	82.1	0.45	98.4
	7.1	12.0	72.7	6.4	61.9	7.29	73.5

The data in **Table 4** indicate that in the case of **preozonation** color, turbidity and biomass reduction are 1.2; 1.4 and 1.4 times higher than in the case of **prechlorination. The formation of THM will be totally avoided.** Among of the different algae species the highest degree of reduction (71-84%) was achieved for blue-green algae. The most resistant towards ozone were diatomite algae with strong shells (reduction degree 15-34%). It was also established that with increasing of turbidity the color reduction diminished - it seems that dissolved ozone decomposes the suspended solids first and only after that reacts with dissolved humic substances. Preozonation was especially effective treatment method for clear cold water, where the ozone solubility is high, the disturbing impact of suspended solids is missing and usual coagulation is not satisfactory, i.e. under winter conditions.

Usage of the GAC filtration after preozonation, coagulation and clarification can reduce the color below 5 deg. and is a guarantee of production of the drinking water of a very good quality by all of the parameters in the Estonian and EEC standards: **color of treated water 0-5 deg., turbidity 0-0.24 g/m^3, COD$_{Mn}$ 1-2 g/m^3, no THM.**

Conclusions

1. Preozonation has remarkable advantages as compared to prechlorination of Lake Ülemiste water viz. significant reduction of THM formation potential, color, turbidity, biomass content and improvement of drinking water taste and odor.
2. Lake water decoloration process with ozone proceeds in the regime of a fast chemical reaction and is limited by the conditions of ozone mass transfer, not by the contact time. With increasing of pH the decoloration effect diminishes. The same impact has the turbidity.
3. Optimum preozone dose should be in the range of 4-10 g/m^3 depending on the season (raw water quality).These values should be checked up during the full scale tests before putting the ozonation station into operation.
4. GAC filtration after preozonation, coagulation and clarification is a guarantee of production of safe drinking water of a very good quality.

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