

AOPs for degrading metaldehyde in surface water used for drinking water

Intensive farming and the associated use of pesticides is one of the main reasons that these regulated substances can be found in the drinking water reservoirs of a large number of British water utilities.

The substance metaldehyde contained in slug pellets is a special challenge for the water utility as this substance is able to easily pass through the conventional treatment steps (ozonization + activate carbon) [1].

In order to check whether so called Advanced Oxidation Processes (AOPs) are suitable for reducing metaldehyde below the limit value, an eight-month pilot phase was conducted on site. The following AOPs regarding degradation of metaldehyde and possible formation of the by-product bromate were investigated:

1. Ozone+ hydrogen peroxide
2. UV light from low pressure lamps + hydrogen peroxide
3. Combination of ozone + hydrogen peroxide and UV light

EMPLOYED REACTORS AND TEST ARRANGEMENT

For evaluating the efficiency of the individual processes, two pilot plants were set up on the premises of the water utility. The plants were supplied with water from the pre-filtering process.

Ozone AOP Pilot plant

The ozone AOP pilot plant was specially designed for employment in water containing bromide aiming at preventing or reducing respectively the oxidation of bromide to bromate by applying a special process. The essential components of the system (ozone generator, hydrogen peroxide dosing, measuring devices, reaction system, degassing and residual ozone destructor) were installed in an insulated container. The oxygen supply was provided by a bundle of cylinders externally set up.



Fig. 1 Ozone pilot container, exterior view

The ozone reactor installed in the container was designed in that way that local excess dissolved ozone does not develop at any time of reaction — a requirement to prevent the formation of bromate. Fig. 2 and 3 show the reactor. Dosing of the hydrogen peroxide takes place in the inlet and will then be intensively mixed with the water to be treated by a downstream static mixer. Then the ozone is only partially fed into the water phase by means of a specially designed mixer. Following the mixing in, the reaction takes place in the downstream pipe section. After the ozone reaction is completed, another mixing element follows and transfers again only a defined part of the ozone into the water phase. Followed by another mixing in, a further reaction zone is passed through. This procedure is repeated five times through the whole reactor so that finally the totally dosed amount of ozone has been mixed in and reacted. Following the last reaction zone, an extended nominal diameter of the pipeline allows reduction of the flow velocity and thus separation of the gas. Possible residual ozone in the gas will be transformed to oxygen by means of a catalytic ozone destructor.

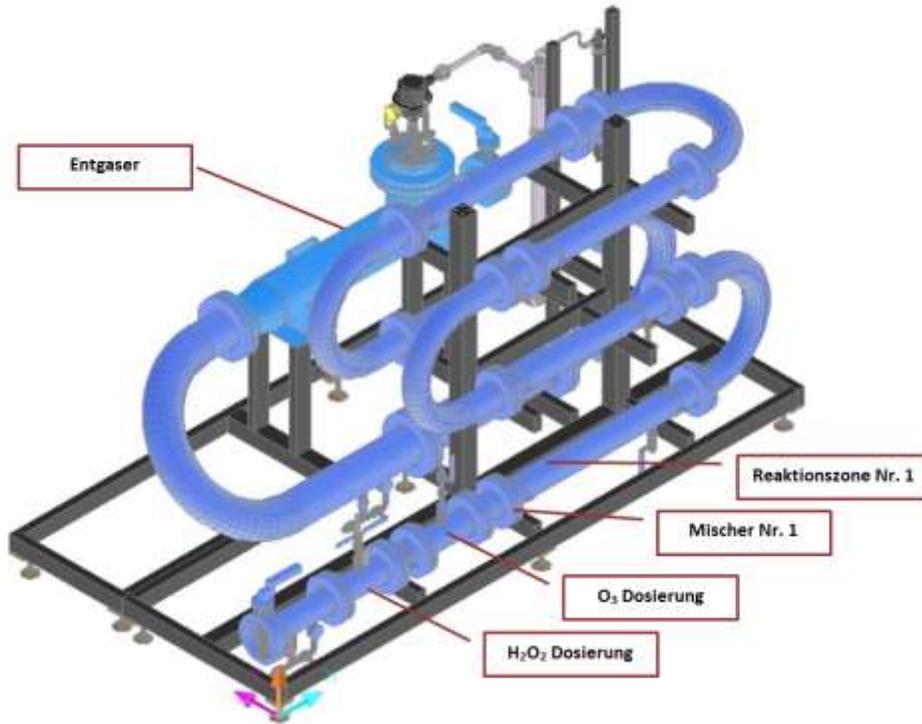


Fig. 2 Ozone reactor

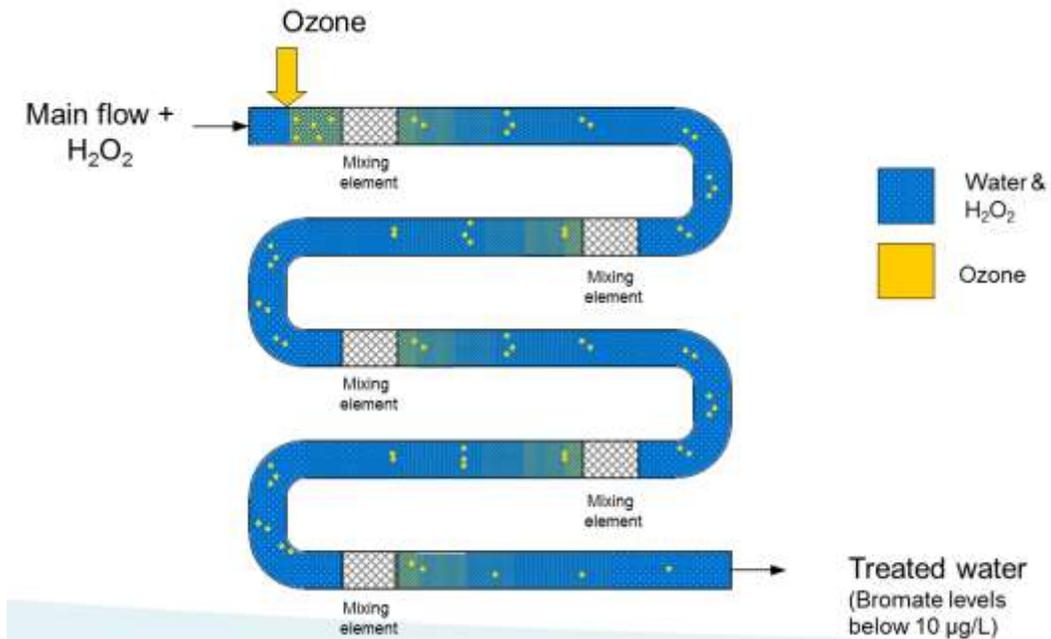


Fig. 3 Functional principle

The reactor was operated with a flow rate between 30 and 40m³/h. The ozone dosages varied between 2 and 13 g/m³.

UV AOP Pilot plant

The reactor employed for the UV AOP was designed to apply high UV doses and to ensure high irradiation intensity in the entire reactor chamber. The UV low pressure reactor is equipped with 3 lamps à 80 watt and a mechanical wiper to remove any fouling from the quartz sleeve surface.



Fig. 4 UVAOP plant

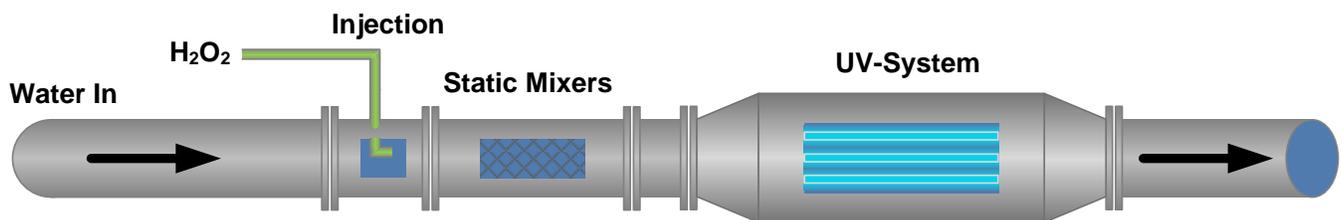


Fig. 5 Procedure UV AOP plant

The hydrogen peroxide required for the AOP is dosed upstream the reactor and homogenized by means of a static mixer. The actual AOP takes place in the irradiation field of the reactor.

Test set-up for the combined AOP

For combining the ozone AOP and UV AOP a partial flow of the effluent from the ozone reactor was led through the UV AOP system. By varying the flow rate various UV doses were realized. Both processes were combined to determine the highest possible reduction of metaldehyde by simultaneously meeting the bromate limit value of 5 µg/L.

Test arrangement

For the test, a partial flow was taken from the pre-ozonized filtered water and fed into the ozone AOP pilot plant with a flow rate of 30 - 40 m³/h. The utilized water was characterized as follows:

TOC	5	mg/L
Conductivity	466	μS/cm
Hardness	207	mg CaCO ₃ /L
Bromide	80	μg/L
Bromate	<5	μg/L
pH	8	
UVT	88	%

Table 1 Water characteristics

In order to make sure that adequate concentrations of metaldehyde are detectable in the untreated water, metaldehyde was added artificially. Concentrations between 0.25 - 4.0 μg/L were set.

RESULTS OZONE AOP

For evaluating the ozone AOP various ozone and hydrogen peroxide doses were set and the degradation of metaldehyde and formation of bromate was investigated. In order to avoid the formation of bromate above the limit value, hydrogen peroxide is provided in abundance. The proportion of ozone to water peroxide is the crucial factor for a possible prevention of bromate formation.

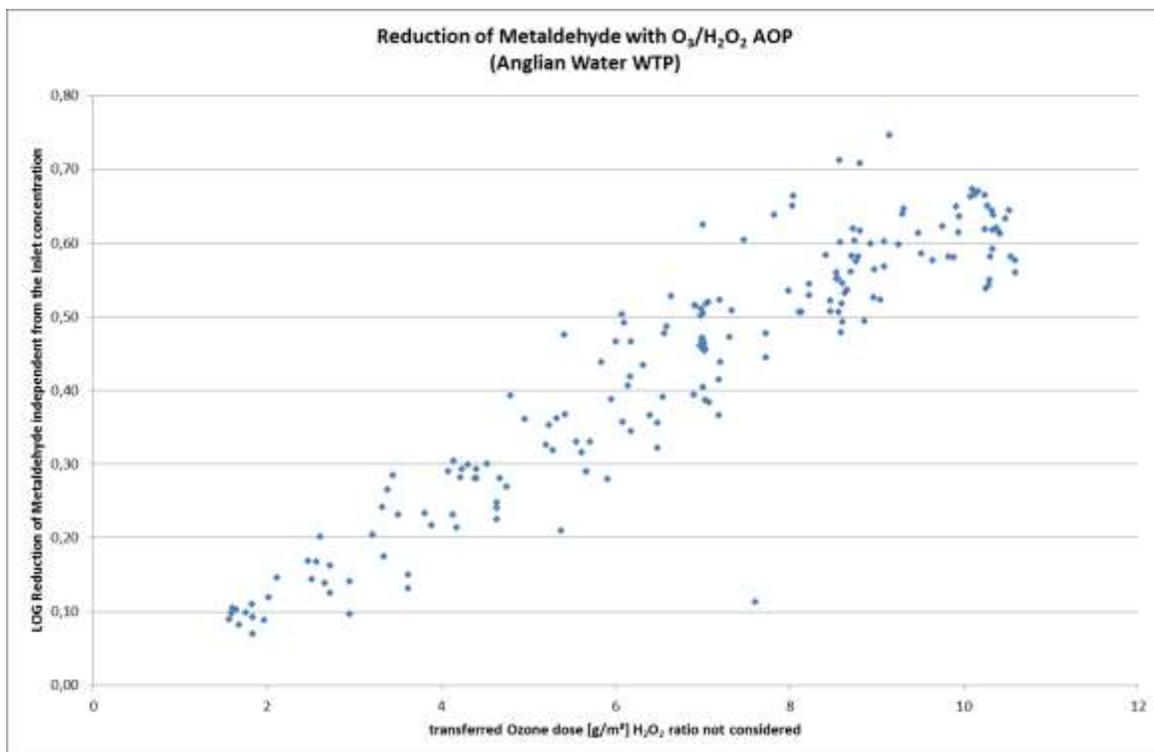


Fig. 6 Degradation of metaldehyde in correlation to the ozone dose

Figure 6 shows the dependence of the degree of degradation of the metaldehyde on the applied ozone dose. The influence of the relation ozone/H₂O₂ has not been taken into account and can be considered as negligible as the hydrogen peroxide was constantly dosed in abundance.

The influence of the metaldehyde concentration in the influent also remains unconsidered in this diagram since the LOG reduction (decade logarithm of the quotient of the inlet concentration to the outlet concentration) is independent of the present original concentration in the analyzed range (0.1 – 3 µg/L) as far as AOPs are concerned.

A linear trend allowing a statement on the necessary ozone dose to achieve a particular required reduction is clearly visible. A desired metaldehyde reduction of 0.5 LOG (70%) with an ozone dose of 8 g/m³ and correspondent dosing of hydrogen peroxide could be demonstrated in all cases.

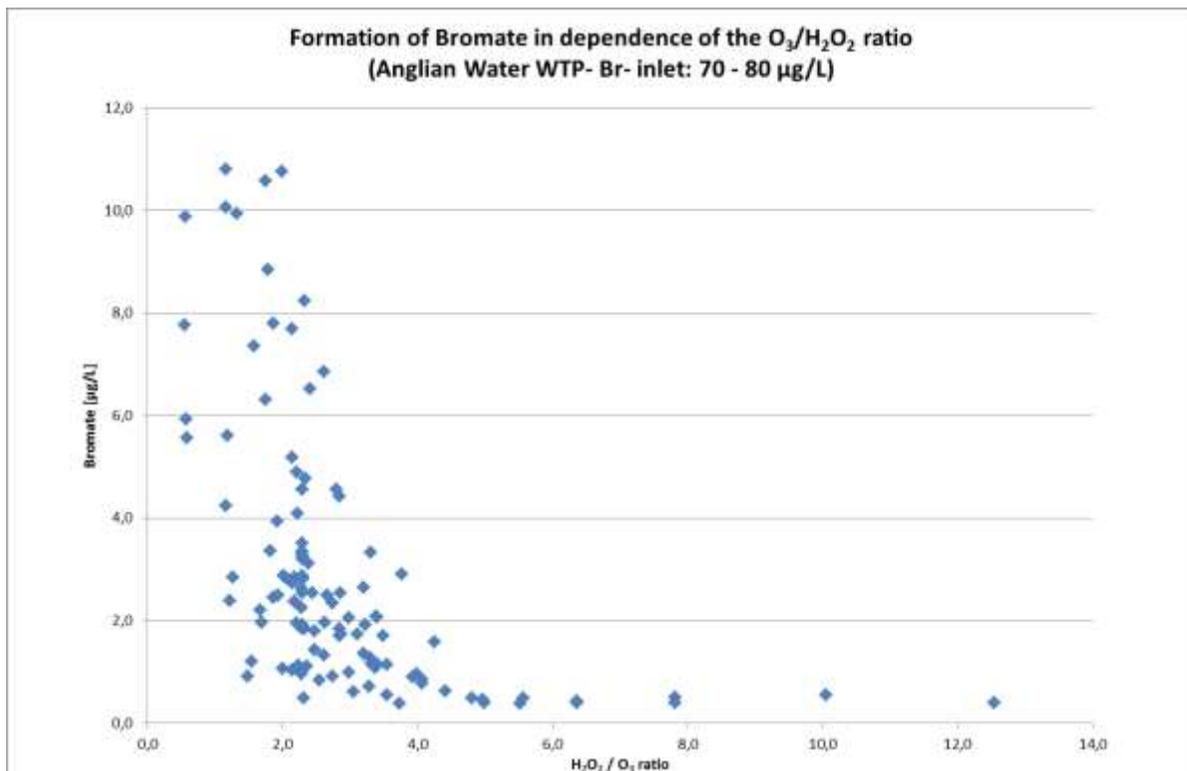


Fig. 7 Bromate formation depending on the proportion ozone / hydrogen peroxide

In addition to the efficient degradation of the target substance, another crucial factor for the feasibility of the ozone AOP to reduce the metaldehyde is the reliable adherence to the limit value of bromate of 5 µg/L. Figure 7 shows the measured bromate formation in dependence on the applied proportion O₃/H₂O₂. It clearly shows that a proportion of at least 3 is to be set for a reliable adherence. That means that a dose of hydrogen peroxide of 24 g/m³ would have to be provided with an ozone dose of 8 g/m³.

To assure these findings, these settings were repeated for several times. In a second test program the focus was on reducing the metaldehyde by 0.5 LOG (70%) and a maximum bromate formation of 3 µg/L. The results are shown in figure 8 and 9.

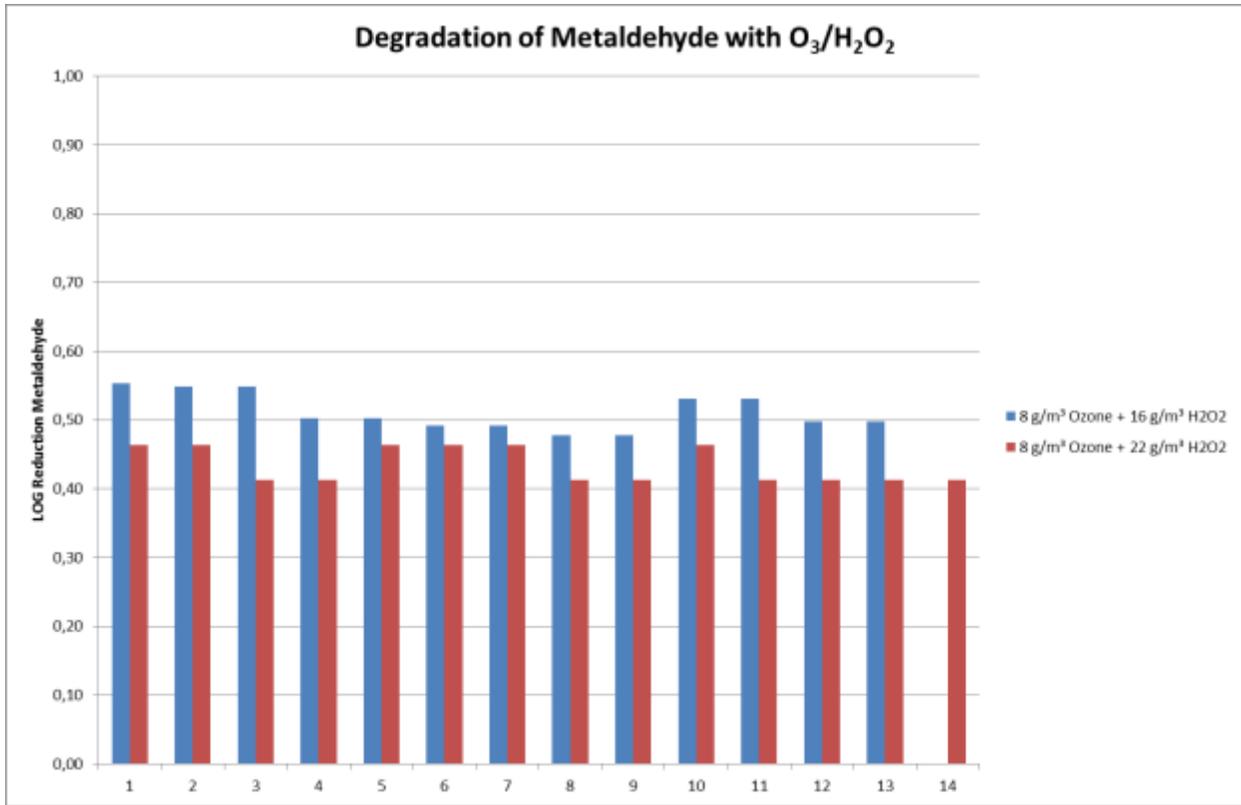


Fig. 8 Degradation of metaldehyde with an ozone dose of 8g/m³ and varying H₂O₂ dose

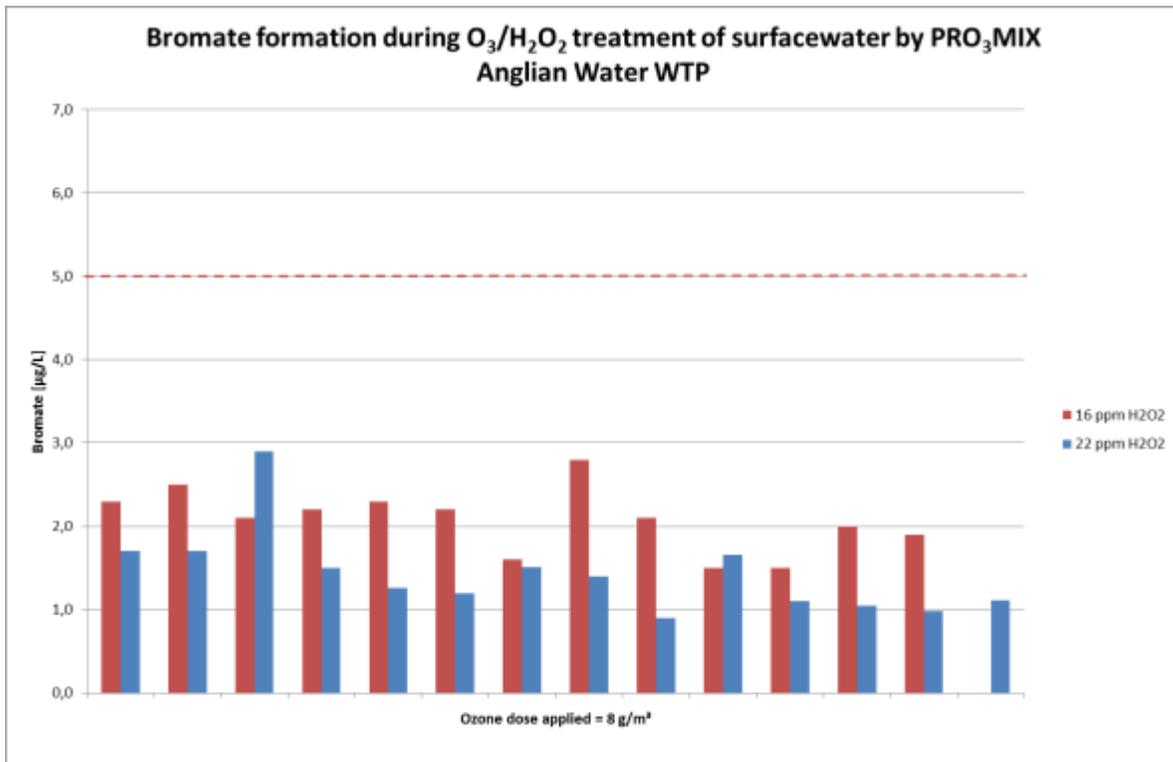


Fig. 9 Formation of bromate with an ozone dose of 8g/m³ and varying H₂O₂ dose

The results reveal that metaldehyde is reduced between 0.4 and 0.5 LOG when applying an ozone dose of 8g/m³ and a proportion of ozone / hydrogen peroxide of 2 - 2.5.

In order to reliably reach 0.5 LOG, the dose would have to be slightly increased accordingly. On the whole it can be noticed that the setting with the lower dose of hydrogen peroxide achieves better results of degradation. This may be influenced by the fact that hydrogen peroxide itself reacts with OH radicals which consequently are no longer available for degrading metaldehyde.

The formation of bromate was prevented with all the tested settings. The value was below 3 µg/L in all cases, the setting with the higher proportion showing a slightly lower formation of bromate.

RESULTS UV AOP

In order to determine the effectiveness of the UV AOP, various UV doses with two different doses of hydrogen peroxide were set. The variation of the applied UV dose was achieved by setting different flow rates. By doing so, the retention time of the water in the reactor is influenced having a direct impact on the dose. The flow rates were set between 0.3 - 0.6 m³/h. The formation of bromate was not investigated in this test arrangement since an oxidation of bromide to bromate by hydroxyl radicals does not take place [2].

Figure 10 shows the degradation of metaldehyde depending on the applied UV dose and concentration of hydrogen peroxide.

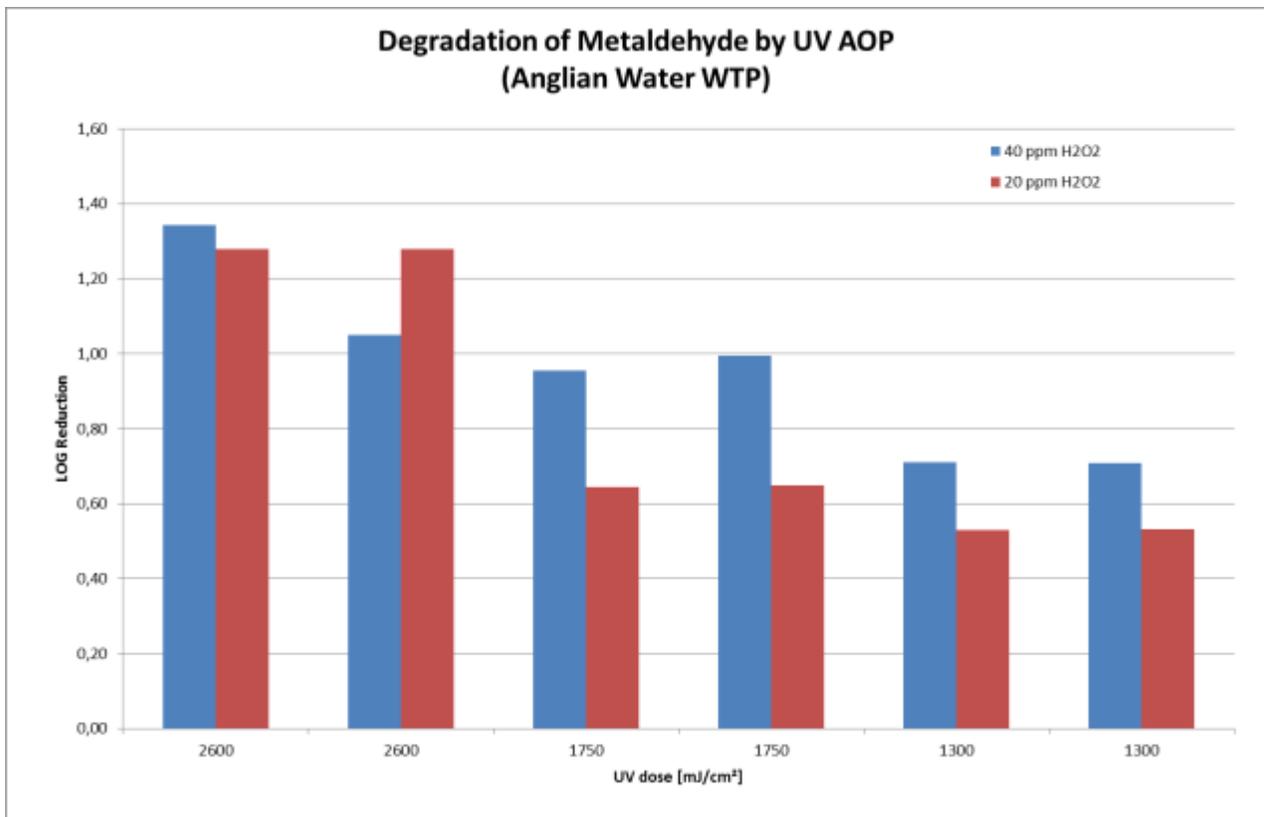


Fig. 10 Degradation of metaldehyde by UV AOP

It can clearly be seen that the degree of degradation of metaldehyde rises when increasing the UV dose. A higher dose of hydrogen peroxide results in a clearly better degree of degradation with lower doses whereas there is no significant difference with higher doses. The reason for this is, among others, that the

measured concentrations of metaldehyde are already close to the quantification limit with a reduction of 1.2 LOG (93%). For a reduction of metaldehyde of 0.5 LOG a UV dose of 1300 mJ/cm² with a dose of H₂O₂ of 20 ppm would have to be applied.

RESULTS COMBINED AOP

In order to obtain reduction rates higher than 0.5 LOG without exceeding the bromate limit value at the same time, the ozone AOP was combined with the UV AOP in a third test arrangement. The aim was to combine the benefits of both AOP technologies in that way that the resulting process can be operated considerably more economically and more safely than the individual process. First the water was treated in the ozone AOP plant. Then a partial flow was led through the UV AOP system. Figure 11 shows the degradation rate of metaldehyde in dependence on the applied UV and ozone dose.

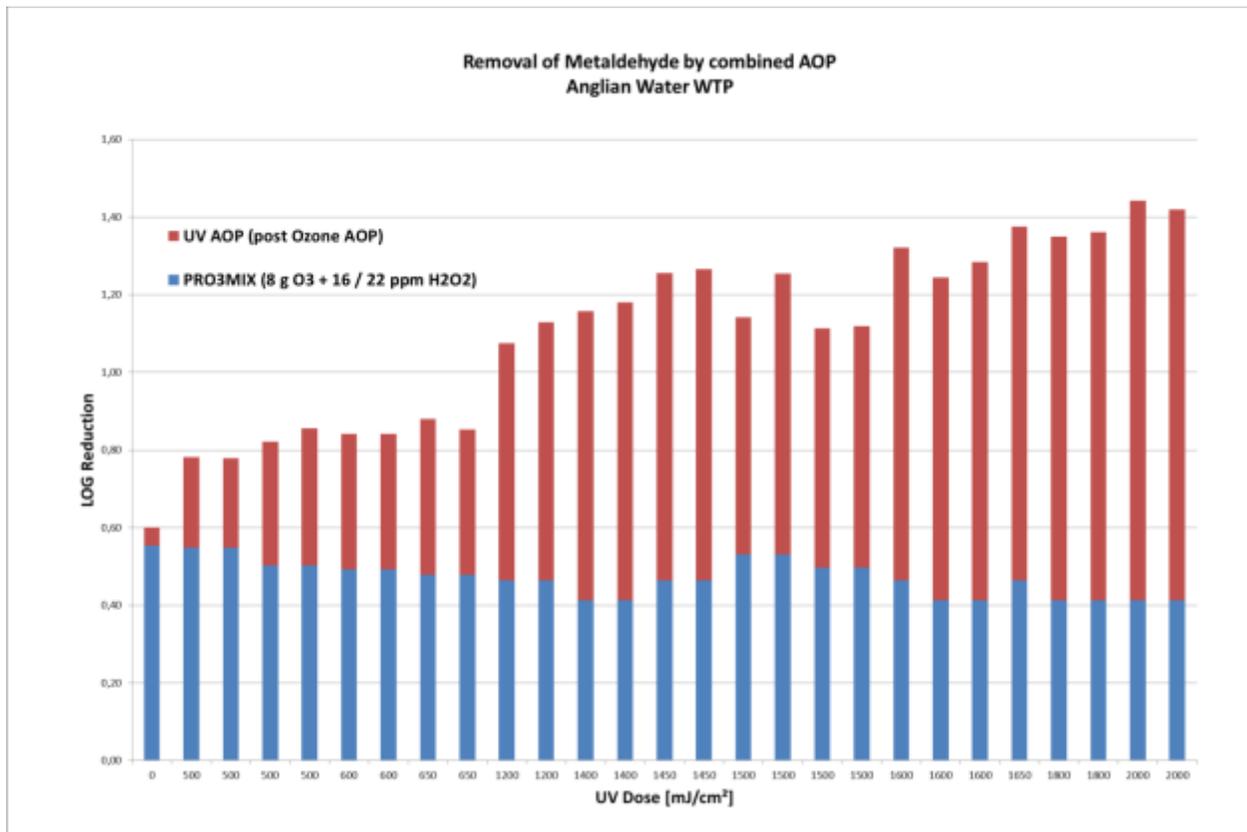


Fig. 11 Degradation of metaldehyde by ozone and UV AOP

By combining both processes very high degrees of degradation can be reached without exceeding the bromate limit value, e. g. when increasing the ozone dose.

The necessary UV dose is also considerably lower than with the only UV AOP. For a reduction of metaldehyde of 1.0 LOG (90%), an ozone dose of 8 g/m³ and a UV dose of 1200 mJ/cm² would have to be chosen instead of a UV dose of 2600 mJ/cm² with the conventional UV AOP. Thanks to these reductions the combined AOP should be able to be operated more cost-effectively than the UV AOP. In order to verify this assumption, the results of the tests were taken to create a large-scale plant design, and the costs for purchasing and operating the plant for a period of 20 years were calculated.

RESULTS COST ANALYSIS

First, assumptions must be made for the cost analysis to reflect the situation in the water works concerned as well as the locally applicable prices for operating resources. The assumptions are listed in table 2.

Oxygen	0.17	€/Nm ³
Hydrogen peroxide	0.90	€/kg
Electricity	0.09	€/kWh
Interest rate for capital	4	%
Depreciation period	20	Years
Flow rate	800	m ³ /h
Operating time	8760	h/a

Table 2 Assumptions for cost analysis

Assumptions for investment costs and costs for required spare parts like UV lamps and electronic ballasts cannot be shown here as they are based on internal figures of *Xylem Services GmbH*.

The result of the analysis is shown in figure 12. Due to confidentiality reasons, a detailed breakdown of capital cost and maintenance cost cannot be shown here.

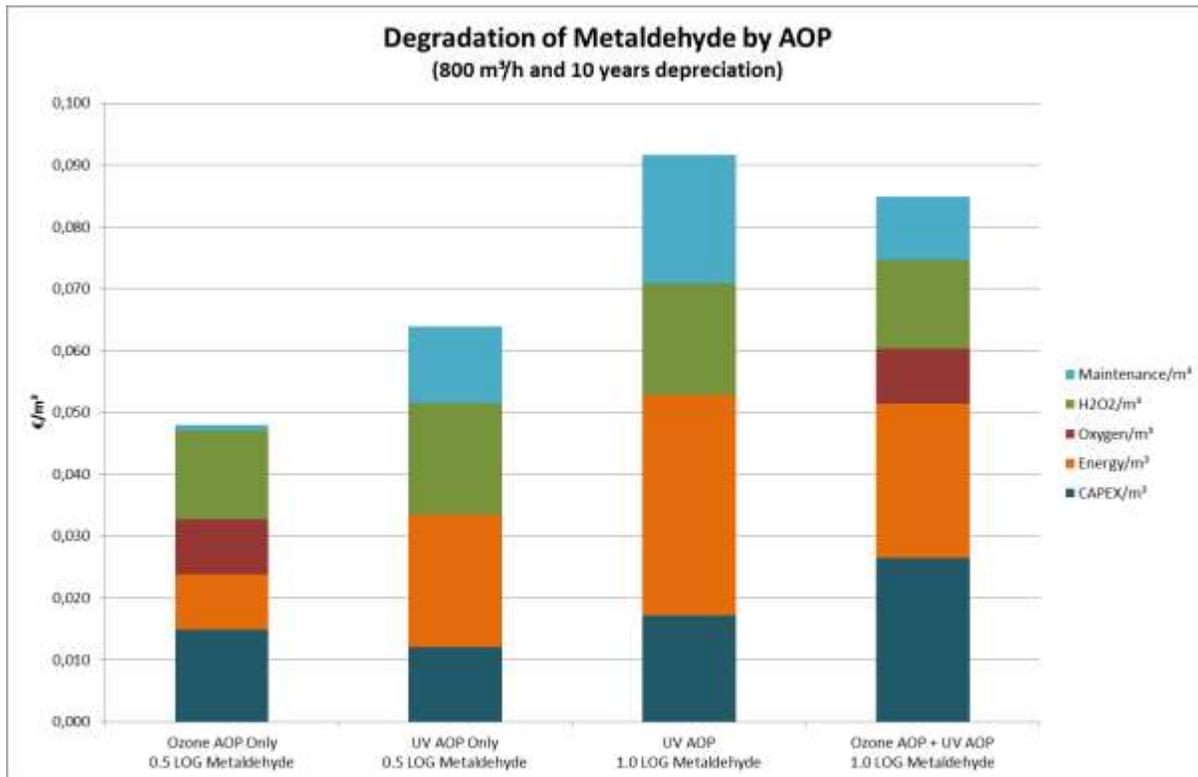


Fig. 12 Cost analysis

The cost analysis confirms the assumption that the ozone AOP is the most cost-efficient option when it comes to reduce 0.5 LOG of metaldehyde. Applying this solution, the costs amount to 4 (euro)cent / m³ treated water.

As for the high reduction of 1.0 LOG, the combined AOP is the most interesting option in business terms since cost savings of about 77 000 euros/a can be realized.

It should also be considered that an AOP based on a combination of ozone and UV technology offers an especially robust barrier for a number of micro-pollutants since both substances reacting selectively with ozone as well as substances being solely degraded by photolysis will be efficiently eliminated [3].

CONCLUSION

By using a specially designed ozone reactor and employing an ozone based AOP, bromate formation can be prevented to the extent that this process allows for being applied in drinking water. The ozone based AOP in this case offers the most cost-efficient technology and allows for realizing significant savings. However, it is not possible to deduce an overall statement from the test arrangement described herein. Each individual case requires a detailed examination as changes in conditions may make the applicability of an ozone based AOP difficult (very high bromide concentrations), or due to the operating method and a very high UV transmittance a UV based AOP may be the best solution.

Therefore, the user of a large-scale plant will be required to test the different technologies for feasibility. Significant cost savings can be realized by such a procedure. A careful selection of the process can guarantee a high level of operational reliability, even if new undesired substances occur.

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