

**AOX AND COD REMOVAL FROM LANDFILL
LEACHATES WITH OZONE AND RADICAL REACTIONS**

Extract from the

PROCEEDINGS

of the

ELEVENTH OZONE WORLD CONGRESS

SAN FRANCISCO 1993

AOX and COD Removal from Landfill Leachates with Ozone and Radical Reactions

Dr. Rüdiger Kaulbach
OZONIA LTD, Switzerland

ABSTRACT

Ozone is the strongest practical oxidant available for water treatment processes. The effectiveness of ozone is the result of two phenomena:

- Solubility of ozone in water (transfer gas-liquid)
- Interactions between organic matter and oxidant

The versatile chemical oxidation and disinfection characteristics of ozone have been used for many different processes in connection with water treatment. Depending on the organic load and the chemistry of the leachate, the ozone oxidation process can be adopted to reduce stable chlorinated organic compounds which form the AOX in leachates from domestic landfills. Leachates with COD values of 3000-5000 mg/l and an AOX value of 3-5 mg/l require the most effective oxidation processes, or combinations of chemical processes available.

For the purpose in question, the oxidation potential of ozone (+2.07 V) is only exceeded by the OH° radical (+2.8 V) which is formed by one of the following reactions:

- combination of $\text{O}_3 + \text{UV}$
- combination of $\text{O}_3 + \text{H}_2\text{O}_2$
- combination of $\text{H}_2\text{O}_2 + \text{UV}$

The paper deals with the State of the Art of process combinations and evaluates the practicability and market acceptance of these systems.

INTRODUCTION

The chemical oxidation with ozone is an innovative technology for the treatment of effluents which are contaminated with organic chemicals, because this process is capable of converting the organic contaminants completely to carbon dioxide if desired. Ozone alone, or in combination with OH° radicals is effective against most organic compounds, and the chemicals used in this process decompose to harmless and even beneficial by-products.

The main objective of treating leachates from domestic landfills is to reduce the COD and AOX load, particularly the persistent portion which is not removed during a

biological pretreatment. Compared to technical alternatives, e.g. adsorption on activated carbon or reverse osmosis, chemical oxidation is a method which produces practically no residues which are to be further handled or discharged. The practicability of this method is now beyond the verge of commercial scale application. The systems which are available today are based on the latest ozone production technique with high ozone concentrations of 12 wt% and more, combined with new findings in water treatment technology. Due to such developments these processes are now becoming more cost effective and reliable than earlier anticipated.

1. DEFINITION OF THE PROBLEM

New regulations for the discharge of leachates from domestic landfills in countries like France and Germany require a State of the Art technology to treat such effluents. The degree of contamination for these effluents is characterised by the following main parameters:

- COD in a range of 1000 - 5000 mg/l
- BOD₅ in a range of 500 - 1000 mg/l
- AOX in a range of 1000 - 3000 µg/l
- NH₄-N in a range of 1000 - 2000 mg/l

The typical effluent volume from a landfill site is 2 - 10 m³/h. In order to comply with legislation for the discharge of waste water, the following threshold values are - expressed in a simplified manner for the example in Germany - the aim of the cleaning technology:

- COD < 200 mg/l
- BOD₅ < 20 mg/l
- AOX < 500 µg/l
- NH₄-N < 50 mg/l

Since the major portion of the contaminants are either biodegradable or oxidizable, the most common treatment method is a one or two stage biology followed by an effective ozonation stage, where ozone is applied in a dosage quantity of several kilograms per cubic meter.

2. BASICS OF CHEMICAL OXIDATION

For any oxidation process the electrochemical oxidation potentials must be considered.

OXIDANT	OXIDATION POTENTIAL (V)
Fluorine (F)	3.03
Hydroxyl radical (OH°)	2.8
Oxygen atom (O)	2.42
Ozone (O ₃)	2.07
Hydrogen peroxide (H ₂ O ₂)	1.76
Permanganate ion (MnO ₄)	1.67
Chlorine dioxide (ClO ₂)	1.15
Chlorine (Cl ₂)	1.36

Tab. 1: Oxidation potentials

The values in table 1 demonstrate clearly that ozone has the highest rate compared to other oxidation agents which are suitable for application in water technology. Only the OH° radical exhibits a stronger oxidation behaviour than ozone alone.

The direct reaction of ozone with a solute M can be expressed as

$$M + \eta O_3 \rightarrow M_{\text{oxide}} \quad /2/$$

where η is the stoichiometric factor for the number of ozone molecules consumed per molecule M transferred to M_{oxide} . This value lies typically in the range between 1 and 5 /2/. Particularly in the case of leachate compounds the factor is very often between 2 and 3.5.

COD and AOX are sum parameters which are characterised by a great variety of individual organic compounds, where most of the organics show a fast reaction with the ozone molecule. Only a small quantity of organics, for example halomethanes, require an advanced oxidation by OH° radicals.

A convenient method of producing OH° radicals is by combining ozone and hydrogen peroxide, which is also known as the Perozone® process /1;4;5/. The stoichiometry is represented by the following reaction:



This reaction provides an additional powerful oxidant with which the effect of mineralisation of the organic matter can be enhanced. However, the OH° radical is much less selective than ozone and its half-life is very short, especially in the presence of scavenging agents like HCO₃⁻ / CO₃²⁻ /1/.

3. PRACTICAL RESULTS FROM BENCH SCALE TESTS

3.1 Oxidation of untreated effluent

The first example of a lab scale leachate treatment considers a typical raw effluent from a domestic landfill site. Similar analysis can be found in many raw waters from landfills. The initial concentrations were :

- COD : 950 mg/l
- AOX : 750 µg/l
- NH₄-N : 980 mg/l
- pH : 7.35

These data represent a “point” measurement, and not average values.

Both curves exhibit a fast degradation of the oxidizable substances and indicate that the required outlet value of 400 mg/l (for indirect discharge) can be achieved after a treatment time of 1.5 hours under batch scale conditions. AOX is also partially destructed (< 0.5 mg/l) and NH₄-N is reduced by 80 % during ozonation.

The addition of peroxide results in a diminished retention time and an improved ozone transfer rate, an effect which was already noticed by other authors /4/.

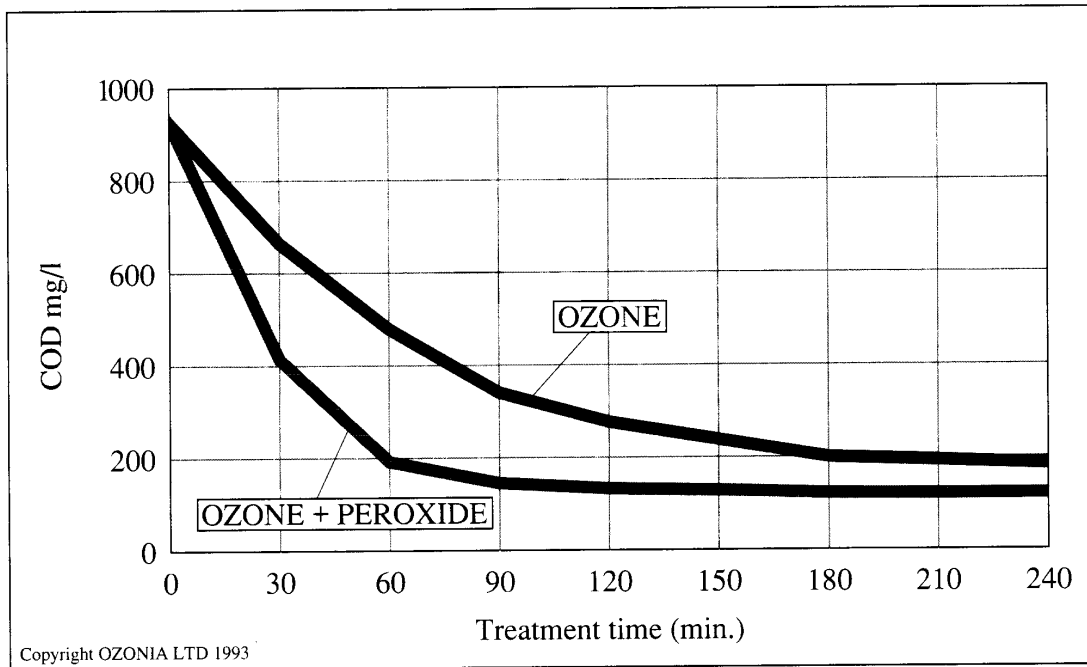


Fig. 1: COD removal during oxidation with ozone and ozone / peroxide.

3.2 Oxidation of biologically pretreated effluent

The second example describes the treatment of a landfill leachate effluent from a typical location, where the contaminated water is already pretreated by an efficient two step biology.

Due to the high load of the raw leachate, the outlet of the biological pretreatment (which removes about 50 % of initial COD) has yet the following composition:

-	COD	=	1000 mg/l
-	AOX	=	2 mg/l
-	NH ₄ -N	<	20 mg/l
-	pH	<	8.5

4. ECONOMICAL CONSIDERATIONS

Derived from many lab scale investigations and results, recently confirmed during pilot tests with a containerised, mobile pilot station, the cost evaluation for the chemical oxidation can be estimated on the basis of an example which is closely related to a situation as described under 3.2.

For a Δ COD of 800 mg/l an ozone dose of approximately 2.4 kg/m³ is required. Assuming a volume to be treated of 5 m³/h, the total capacity of the ozone installation is 12 kg O₃/h.

The specific consumption figures are :

Oxygen:	08.3 - 00 kg/ kg O ₃
Energy:	13.0 - 14 kWh/ kg O ₃

The annual treatment costs on a 8000 hours operation basis and specific costs for oxygen of DM 0,22/kg O₂ and energy of DM 0,15/kWh are (calculated on price conditions which are usually in Germany) :

8000 h	x	5 m ³	x	4,38	=	DM 175 200.-/a oxygen costs
8000 h	x	5 m ³	x	5,04	=	DM 201 600.-/a energy costs
						<hr/>
						= DM 376 800.-/a consumption costs
						= DM 9.42/ m³ treatment costs

The total treatment costs, including investment depreciation, operation and maintenance are very often in a range of 20 - 30 DM/m³.

Treatment costs in this order of magnitude are very competitive compared to alternative methods, which require a multi step procedure consisting of RO, evaporation, drying and underground storage.

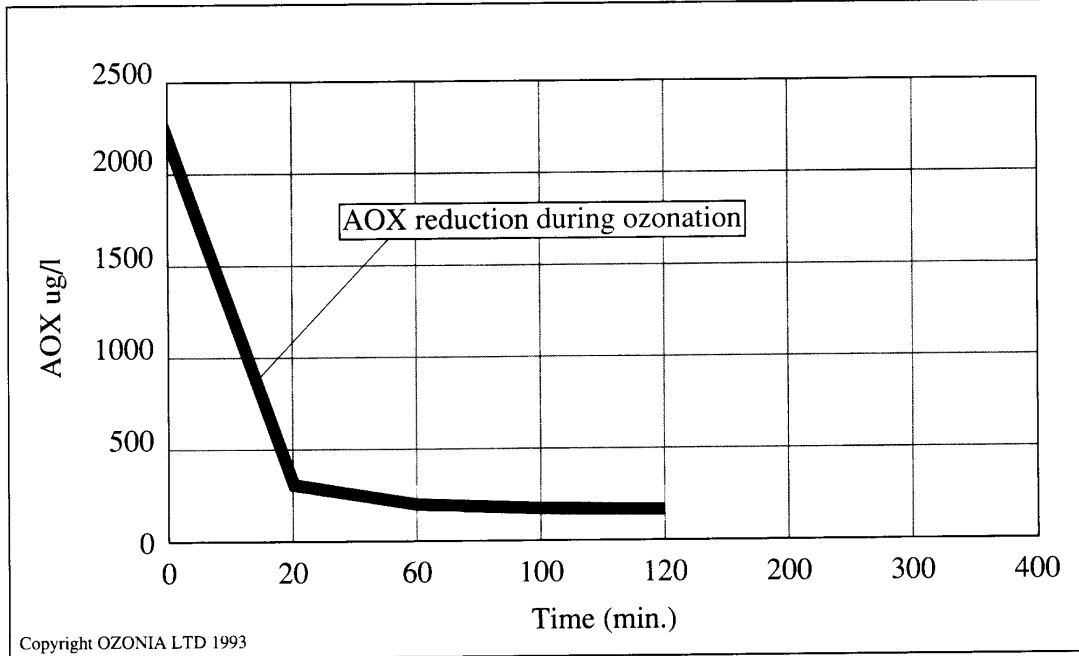
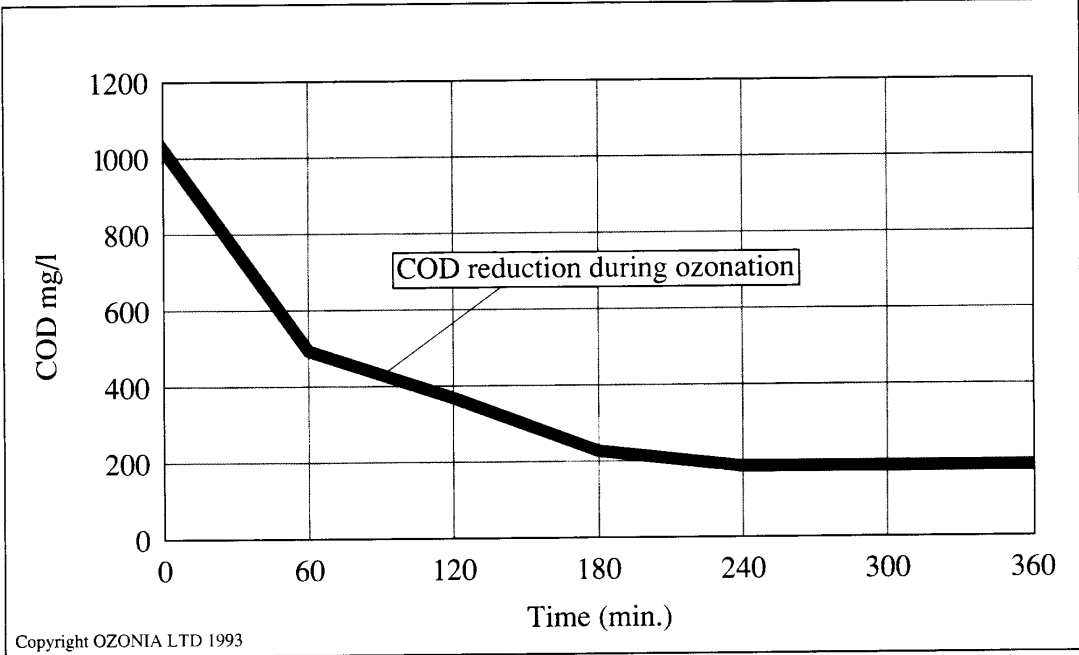


Fig. 2: COD and AOX removal during oxidation with ozone

5. CONCLUSION

Chemical oxidation with ozone and/or H₂O₂ and UV, is an appropriate method for the cleaning and detoxification of highly contaminated effluents like leachates from landfills. The most dangerous portion of the contaminating load, which is summarised under the AOX and COD values, can efficiently be destructed on site, without any „handling“ or transportation hazards and under avoidance of residue formation.

The market acceptance of this technical solution is steadily growing - an estimated total number of about 15 plants which are already in operation or under construction in Germany - confirms this presumption.

REFERENCES

- /1/ von Sonntag, C. : Chemical principles behind the use of UV-radiation and/or oxidants (ozone and hydrogen peroxide) in water pollution control. CUTEC Schriftenreihe, Nassoxidative Abwasserbehandlung, Goslar 1993
- /2/ Hoigné, J. and Bader, H., : Rate constants of reactions of ozone with organic and inorganic compounds in water.
1. Water Research 17, 1983
- /3/ Bailey, P.S., : Ozonation in Organic Chemistry. Vol. 2. Nonolefinic compounds, Academic Press, New York 1978
- /4/ Wable, O. Jousset, M. Courant, P. and J.P. Duguet : Oxidation of landfill leachate by ozone and hydrogen peroxide : A French example. Proceedings of the International Symposium on Ozone-Oxidation Methods for Water and Wastewater Treatment, Wasser Berlin 26. - 28. April 1993.
- /5/ Gilbert, E. : Kombination von Ozon/Wasserstoffperoxid zur Elimination von Chloressigsäure. Vom Wasser 77, 1991.