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The Ecoclear® Process. Results from Full-Scale Installations

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Abstract

Ecoclear®, a heterogeneous catalytic ozonation process, has been in commercial operation since 1992 at an ozone consumption of 1.7 kg ozone per kg COD removed. Chlorinated hydrocarbon concentrations in contaminated groundwater are reduced to less than 10 μg/L. A second full scale installation was commissioned early in 1996 for leachate treatment. It is incorporated in the Biomembrat®-Plus process, a combination of biological treatment, nanofiltration and catalytic ozonation, at an ozone consumption of less than 1.0 kg ozone per kg COD removed.

Introduction

Many organic substances in water are stable towards ozonation. The reactivity of molecular ozone, O_3, is too low to mineralize these substances. To increase the reactivity of ozone it has to be activated, which is called advanced oxidation. The improved performance of advanced oxidation processes generally is explained by the production of reactive free radicals. Ozone can be transformed into OH-radicals using UV-radiation or hydrogen peroxide. OH-radicals are non-selective and are scavenged by components that often are present in wastewater, such as carbonate anion. To avoid the scavenging effect of carbonate ion, a heterogeneous ozonation process, Ecoclear®, has been developed (1), using a special grade activated carbon as the catalyst. It results in a lower ozone consumption and an increased reaction rate. Experimental work on laboratory and pilot-plant scale has been conducted to determine the mechanism (1). This work forms the basis for designing full-scale installations.

In this paper the proposed mechanism is explained, a description of two different full-scale Ecoclear® installations is given and the results obtained are reported. First an installation for groundwater treatment is described. Next a description is presented of an installation for the purification of leachate, where the Ecoclear process is combined with biological treatment, ultrafiltration and nanofiltration.

Mechanism of the Ecoclear® Process

The Ecoclear process is a heterogeneous catalyzed ozonation process. Activation of the oxidation reaction is achieved using a solid catalyst. A solid catalyst can work only if the components to be oxidized are adsorbed at the surface and if the oxidation reaction takes place on the surface using the activated species. The catalyst used in the Ecoclear® process is a special grade activated carbon and contains no heavy metals or other additives.

Activated carbon is well known as an excellent adsorbent for organic molecules. In ozone technology it is also known as a destruction catalyst to remove residual ozone from water. Literature (2) states that activated carbon can form oxygen radicals at the surface from molecular oxygen (O_2). Because oxygen is a stable component, the formation of the radicals only takes place at elevated temperatures (>400°C) (2). Ozone is a much less stable form of oxygen and therefore can be transformed into radicals at ambient temperatures. The radicals formed in the Ecoclear® process are assumed to be the same as the known surface radicals from oxygen, which are $O^{\cdot}$, $O_2^{\cdot}$,$O_3^{\cdot}$ (3). These radicals can react with adsorbed organic components. It has been demonstrated that the surface reactions do not involve OH-radicals (1).

The process comprises a three-phase system: solid, gas and liquid. This means that several transport phenomena combined with different reactions take place together, as illustrated in Figure 1, namely:

- Transport of O_3 from gas to liquid
- Transport of both O_3 and organics to the surface
- Adsorption of the organics onto the surface
- Chemisorption of ozone at the surface
- Reaction between adsorbed organics and the O-radicals
- Desorption of the reaction products from the surface
- Parallel phenomena are:
    - O_2 formation from O_3, which is suppressed kinetically.
    - Stripping of volatile components, which may be absorbed again later in the process.
    - Water phase reactions. These are slow because of the low O_3 concentration in the water phase.

In most cases the amount of ozone needed can be reduced to stoichiometric values. In a large number of pilot-plant experiments with leachate the ozone consumption was close to 1.0 $kg_{ozone}/kg_{\Delta COD}$, which means that all the oxygen atoms from molecular ozone were used in the reaction.

Selective oxidation in the Ecoclear® process is possible depending on adsorption characteristics and reactivity of the components to be oxidized. Differences in the polarity and molecular weight of the organic components result in different adsorption capacities and adsorption strengths. This may result in a chromatographic effect in the Ecoclear® system, similar to those observed in activated carbon processes. Because of this aspect, selective oxidation of non- or slightly polar components is possible.

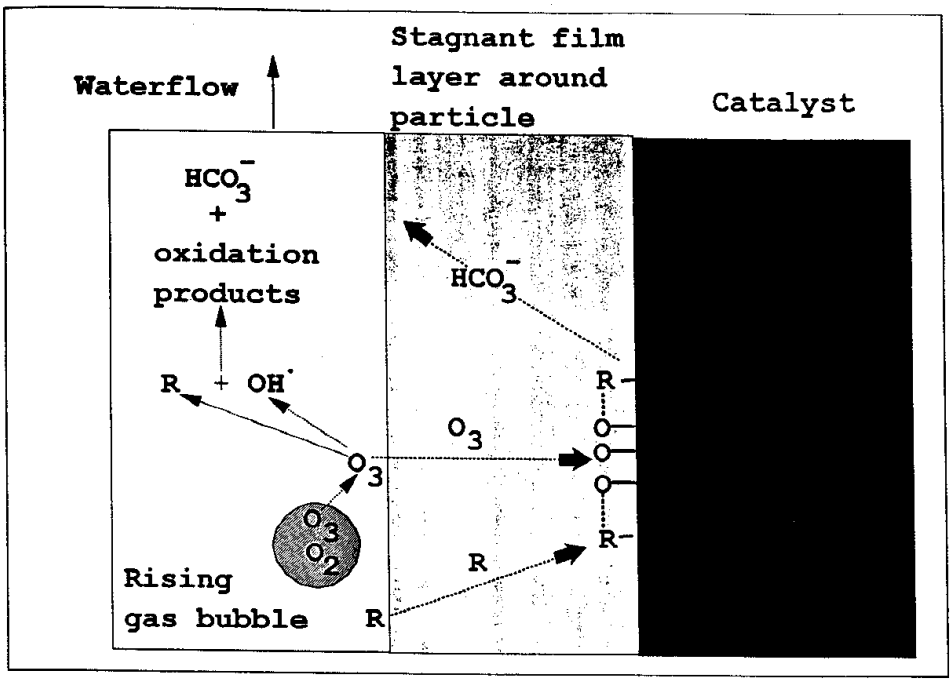

Figure. 1. Various reaction steps.

Full-Scale Installations

A computer simulation model has been developed that takes into account all the known transport and reaction phenomena during steady state situations. The kinetic constants, determined from experimentation, can be used to design full-scale installations. Two different full-scale installations are presented in this section. The first is a stand-alone installation and the second is an example of the integration of Ecoclear®, biological treatment and membrane filtration in one installation

THE ECOCLEAR® PROCESS FOR GROUNDWATER TREATMENT

Chlorinated hydrocarbons have been used widely in the past as degreasing agents in the metal industry. As a result of leaks or spills, these components have found their way into the soil, and as a result the groundwater below a factory has become polluted. The owner of the factory desired to remove the pollution by groundwater withdrawal. The groundwater is pumped up from three different deepwells and is treated before discharge to the sewage system. The following components are present: 1,1,1 trichloroethane (TCA), aromatic components (BTEX) and mineral oil. Since the beginning of 1996 a significant amount of trichloroethylene (TCE) also has been found to be present. A full-scale Ecoclear® installation was started up in 1992. To reach the required effluent quality a residence time of 70 minutes and an ozone dose of 1 kg/h was needed. The ozone is produced from oxygen (LOX) at a concentration of 30 g/Nm^3. A schematic view of the treatment plant is given in Figure 2. The total groundwater flow to be treated is 20 m^3/h.

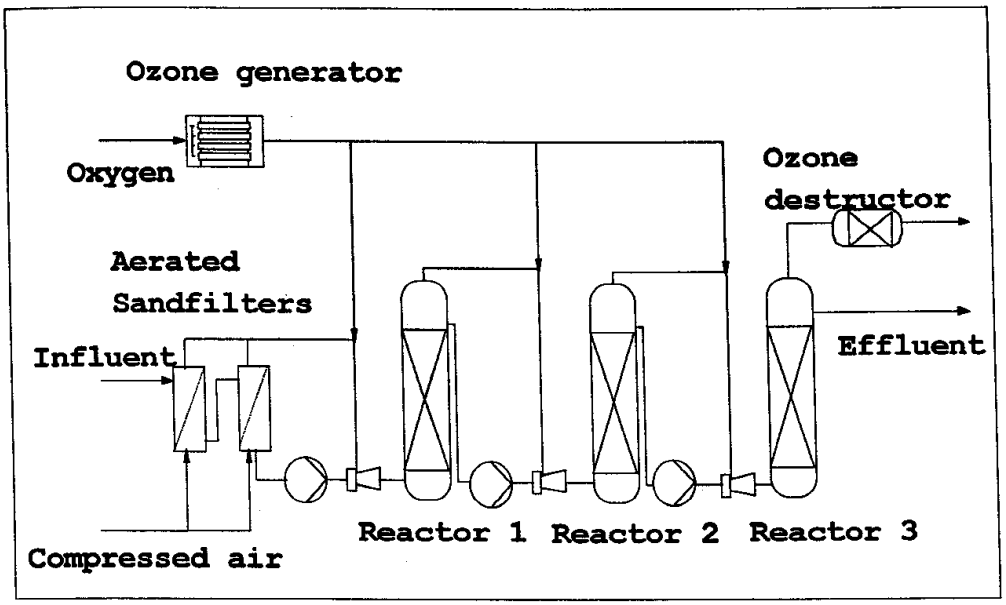

Figure 2. A groundwater treatment plant.

After pretreatment with an aerated sand filter to remove iron, the groundwater is treated in three reactors in series. Off-gas from each of the reactors is brought into the next reactor. Although the off-gas of the final reactor is almost free of ozone, it is still passed through a catalytic ozone destructor. The ozone generator is cooled with the purified groundwater.

In Table I the average concentrations over the period are presented. An ozone dose of 50 mg ozone / L water is required because of the presence of humic acids. This translates to 1.7 $kg_{ozone}/kg_{\Delta COD}$.

TABLE I. AVERAGE RESULTS AFTER TREATMENT IN ECOCLEAR®

Contaminant		Influent	Effluent	Discharge limits
TCA	[μg/L]	400	5	10
TCE*	[μg/L]	180	< 1	10
BTEX	[μg/L]	50	< 0.2	100
Mineral oil	[μg/L]	50	< 50	1000
COD	[mg/L]	40	10	

* Since beginning 1996.

The gas pressure in the ozone generator is insufficient to overcome the pressure drop over the reactors. Therefore a method is needed to increase the gas pressure. Instead of choosing a compressor, a special gas-liquid (mixed phase) distribution system has been designed, using venturi injectors. This system allows mixing of the off-gas from a reactor with make-up gas containing ozone. One of the advantages is that only the off-gas from the last reactor is released and therefore the amount of volatile components in the off-gas is negligible.

As can be seen from TABLE II, the pumps are the main consumers of energy. High pressure pumps are needed because of the venturi-injection system, which has a pressure drop of approximately 8 bar. Future designs primarily will incorporate gas distribution systems based on separate gas and liquid distributors. Pressure drops of the reactors are no longer a design issue, because ozone generators are available which operate at higher pressures, i.e., the Trailigaz MZI series operates at 1.7 barg. In most cases this eliminates the need for venturi injection and reduces the pump energy substantially.

TABLE II. UTILITY CONSUMPTION

Oxygen	[kg/h]	42
Electricity:		
* ozone production	[kW]	8.5
* pumps	[kW]	24
* other	[kW]	2.0

THE ECOCLEAR® PROCESS FOR LEACHATE TREATMENT AS A PART OF THE BIOMEMBRAT®-PLUS PROCESS

Leachate coming from landfills contains a wide range of organic and inorganic components. The level of components in the leachate is too high for discharge to surface water, and has to be purified. Some of the relevant treatment parameters for discharge to surface water in Germany are (Anhang 51):

* COD : 200 mg/L
* BOD_5 : 20 mg/L
* AOX : 500 μg/L
* N-tot : 70 mg/L
* $N\text{-}NH_4$: 10 mg/L
* $N\text{-}NO_2$: 2 mg/L
* P-tot : 3 mg/L

The most common system is a combined anoxic and aerobic biological treatment followed by a polishing step. Ozone is widely used in post-treatment. Conventional aerobic biotreaters need a large surface area, because of the relatively slow removal rates.

The German company Wehrle-Werk AG has developed the Biomembrat®-Plus process (5). It is an activated sludge process operated at increased pressure, 3 barg (6), combined with ultrafiltration, nanofiltration and recirculation of the concentrate from the nanofiltration to the biological treatment. The biosludge is kept in the system by ultrafiltration, and as a result a high biomass concentration can be achieved [up to 25 g/L, (7)]. The pressurized bioreactor results in an increased oxygen supply and efficiency. An increased COD removal rate is achieved, 80-90 % (7), along with a reduced sludge production [0.05 $kg_{dry\ sludge}/kg_{\Delta COD}$, (6)]. The BOD_5 and nitrogen components are completely removed by nitrification and denitrification.

The effluent of the biotreater still contains recalcitrant and non-biodegradable components (residual COD and AOX) after which the permeate is of suitable quality to be discharged

to the surface. The concentrate, containing recalcitrant and non biodegradable components, is treated before it is recirculated to the biotreater. An Ecoclear® process is installed at the German landfill "Berg" to treat the concentrate from the nanofiltration step. Treating the highly polluted concentrate tends to reduce the ozone consumption and to remove the COD and AOX to approximately 50% by partial oxidation. This partial oxidation improves the biodegradability of the organic pollutants. The Ecoclear® installation consists of one reactor with a catalyst volume of 15 m^3 (total reactor volume approximately 25 m^3). The ozone production capacity is 6 kg/h at an ozone concentration of 120 g/Nm^3 using oxygen (LOX).

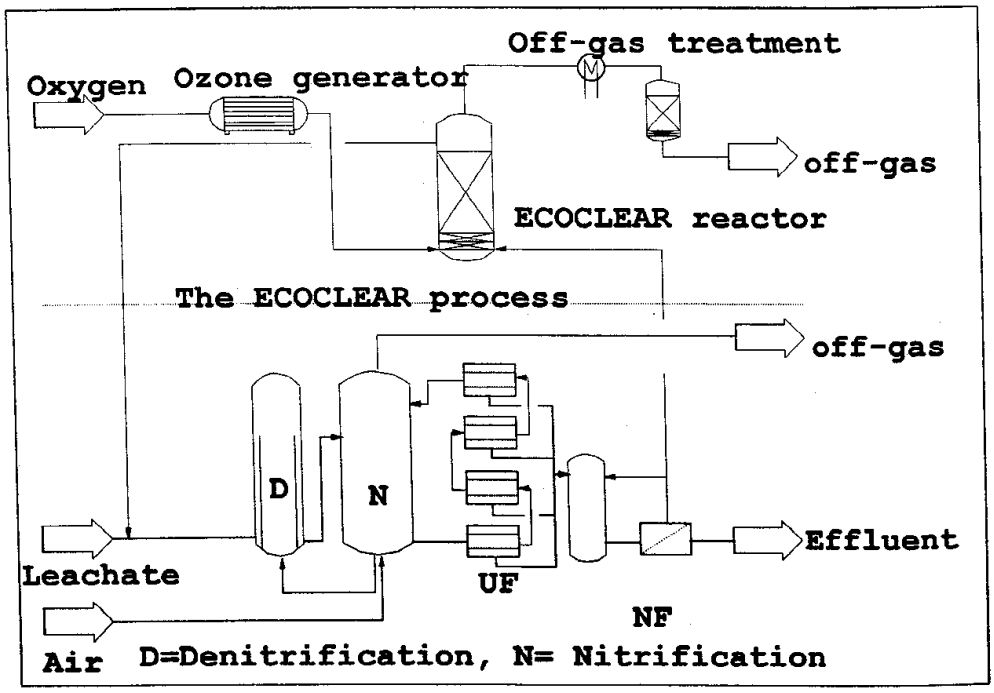

Figure 3. Leachate treatment in the Biomembrat®-plus concept (Wehrle-Werk AG).

The leachate treatment plant has been operating since March 1996. The design data of the Ecoclear® process are presented in Table IIIA and data of the biology and the membrane processes are presented in Table IVB. The actual plant data are presented in Tables IIIB and IVB. The utility consumption under design conditions is presented in Table V.

TABLE IIIA. DESIGN DATA OF THE ECOCLEAR® PROCESS, AT DESIGN OZONE PRODUCTION CAPACITY (4 kg/h)

Design:	Influent Ecoclear® NF Concentrate	Effluent Ecoclear®
COD, mg/L	8,000 - 9,000	2,000 - 3,000
AOX, $\mu g/L$	7,000 - 9,000	500 - 1,000
	Average Flow:	
Flow, m^3/h	0.4	

Optimization of the total plant will be conducted by Wehrle-Werk AG. The unit was started up at an ozone dose of 0.8 $kg_{ozone}/kg_{cod\ in}$.

TABLE IIIB. ACTUAL DATA OF THE ECOCLEAR® PROCESS

		Influent Ecoclear® NF Concentrate	Effluent Ecoclear®
COD	mg/L	5,000	500
AOX	µg/L	4,800	1,000
SK4.3	mmole/L	41.3	34.7
pH		6.5-7	7.5-8
Flow	m^3/h	0.4	
O_3dose	kg/h	1.0	
O_3cons.	$kgO_3/kg_{\Delta cod}$	0.8	

Source: Wehrle-Werk AG

TABLE IVA. DESIGN DATA OF THE BIOMEMBRAT®-PLUS SYSTEM

		Raw leachate	Effluent: Biology	Permeate: NF
COD	mg/L	3,000	900	< 200
AOX	µg/L	2,000	1,200	< 200
N-NH_4	mg/L	1,500	< 5	< 5
N-NO_2	mg/L		< 1	< 1
TKN	mg/L	1,800		
N-inorg.	mg/L	1,500	<50	<50
Flow	m^3/h	1-2.5	1.2-3.1	1.0-2.5

Source: Wehrle-Werk AG

TABLE IVB. ACTUAL DATA OF THE BIOMEMBRAT®-PLUS SYSTEM

		Raw leachate	Permeate: NF
COD	mg/L	3,200	60
AOX	µg/L	2,100	260
N-NH_4	mg/L	730	0.2
N-total	mg/L	930	50
Flow	m^3/h	2.3	2.3

Source: Wehrle-Werk AG

The result of the combination of techniques installed is a compact installation having reduced capital costs and operating cost. The reactor volume of the Ecoclear® installation is small compared to the classical post-treatment applications.

The advantages of the Ecoclear® process in this application are:

- o No oxalate anion is formed.
- o Foaming does not occur because of the presence of the catalyst bed.
- o The dark color of the permeate has no influence on the performance.
- o The increased level of carbonate ion does not influence the performance.

TABLE V. UTILITY CONSUMPTION AT DESIGN CONDITIONS

Ecoclear® (at 4 kg ozone / h):		
Oxygen	[kg/h]	48
Electricity:		
* ozone production	[kW]	40
* other	[kW]	4
Biotreater, UF and NF:*		
Electricity:		
* Biology + Ultra-filtration	[kWh/m³]	18
* Nano-filtration	[kWh/m³]	6
* source: Wehrle werk AG		

Savings in operational costs are made because less ozone is needed. At high COD values for the same amount of COD removed, the ozone consumption is lower than at low COD values. A COD concentration reduction of not more than 50-70% is required for recirculation to the biological treatment whilst operation of the Ecoclear® as a polishing step requires 80% or more reduction in concentration. Both aspects result in a lower ozone capacity to be installed.

The high sludge concentration makes the biotreater less sensitive towards shock loadings in the influent. The Biomembrat®-plus system, biology, membrane systems and the Ecoclear® process provides a cost-effective and reliable system.

Conclusions

1. Ecoclear proved to be a commercial scale, cost-effective, advanced oxidation system. The system is flexible in its combination with other techniques, as demonstrated when incorporated in the Biomembrat®-Plus system to produce a highly efficient solution.
2. On commercial scale the ozone consumption is demonstrated to be low.
3. High conversion levels can be achieved in groundwater treatment.
4. At high concentrations, complete mineralization is possible, if required.

Acknowledgements

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Key Words

Ozone; Catalytic Ozonation; Leachate Treatment; Groundwater Treatment; Ecoclear® Process;

Résumé

Ecoclear®, un procédé d'ozonation en présence d'une catalyse hétérogène, est utilisé à l'échelle industrielle depuis 1992, avec une consommation d'ozone égale à 1,2 kg d'ozone par kg de DCO éliminée. La concentration en hydrocarbures chlorés dans une eau souterraine polluée a été reduite à une valeur inférieure à 10 µg/L. Une deuxième installation à l'échelle industrielle a été réceptionée au début de 1996 pour le traitement des jus de décharge. Elle est combiné dans le procédé "Biomembrat-Plus" incluant traitement biologique, nanofiltration et ozonation catalytique, conduisant à une consommation d'ozone inférieure à 1,0 kg d'ozone par kg de DCO éliminée.

Zusammenfassung

Beim Ecoclear®- Verfahren handelt es sich um eine katalytische Oxidation, die seit 1992 großtechisch eingesetzt wird. Der spezifische Ozonverbrauch liegt bei 1,7 kg Ozon pro kg CSB_{el}. Die chlorierten Kohlenwasserstoffverbindungen in einem kontaminierten grundwasser werden auf weniger als 10 µg/L reduziert. Eine weitere Anlage befindet sich seit Anfang 1996 zur Behandlung von Deponiesickerwasser in Betrieb. Das Ecoclear®-Verfahren ist dabei in das Biomembrat®-Plus-Verfahren integriert, eine Kombination bestehend aus biologische Vorbehandlung, Nanofiltration und katalystischer Oxidation. Durch die Behandlung der Konzentrate aus der Nanofiltration wird ein Ozonverbrauch von weniger als 1,0 kg Ozon pro kg CSB_{eli} erzielt.