

# PLASMA-CATALYTIC TREATMENT OF COMPLEX VOCs IN A GROUND WATER CLEANING FACILITY

K.-P. Francke, H. Miessner and R. Rudolph

IUT GmbH, Institute for Environmental Technologies  
Volmerstrasse 9 B  
D-12489 Berlin, Germany

## ABSTRACT

We report on the plasma-catalytic treatment of contaminated air in field a experiment at a groundwater cleaning facility. 60 m<sup>3</sup>/h of contaminated stripper air were processed in a 1 kW dielectric barrier discharge reactor followed by a low temperature catalytic converter working at 110 °C. Removal rates of at least 85 % were achieved for each of the organic components in the complex mixture of chlorinated hydrocarbons and aromates. The total input concentration was in the range of 100 ppm (C1). The necessary energy density required for the plasma-catalytic process was as low as 12 Wh/m<sup>3</sup> (≈ 43 J/l), which can be related to an equivalent adiabatic temperature rise of ≈ 40 K.

## INTRODUCTION

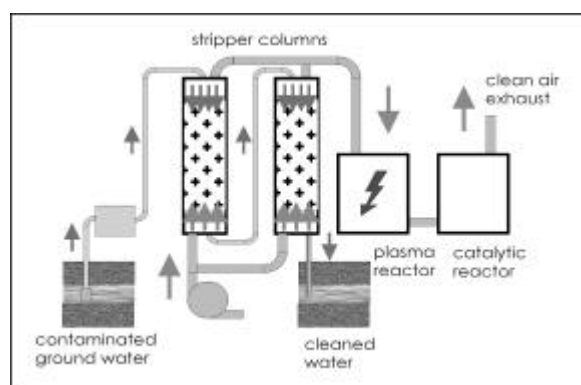
Strong environmental regulations for pollution control forced research work for effective methods to convert industrial off gases into harmless or less toxic reaction products. Depending on pollution type and concentration, thermal or catalytic incineration, filtering by adsorption or absorption, biological cleaning or any combinations of these methods have been used in practice.

The working temperature of the incineration process can be lowered from above 700 °C to 300-500 °C using appropriate catalysts. This catalytic oxidation is advantageous in the case of sufficiently high VOC (volatile organic compound) concentrations, when the exothermic reaction results in a selfsustained process. At relatively low concentrations (<1000 ppm) - as often found in industrial practice - additional heating energy has to supply in order to maintain the catalytic incineration process. So, for low pollution concentrations, gas discharges have been used for removal of toxic components instead of thermal energy as it has been discussed and demonstrated [1].

Plasma based technologies are becoming more and more important for the treatment of various environmental hazards ranging from air pollutants to solid waste [2]. For the control and removal of gaseous pollutants, non-thermal plasmas provide a promising, energy effective technology, especially in the case of low VOC concentrations. If used in combination with appropriate catalysts a remarkable synergetic effect can be achieved [3], resulting in a substantial lowering of the energy demand. This could be shown in small scale laboratory experiments in synthetic or room air contaminated with different organic compounds. The aim of this work was to study the plasma-catalytic cleaning process under field conditions, that means in large flows of humid air, with complex organic loads of halocarbons and aromates.

## EXPERIMENTAL ARRANGEMENT

The field experiment has been carried out on the area of a formerly paint factory. Here a substantial ground water damage from different solvents is currently treated by stripping combined with conventional catalytic incineration. The principle scheme of the



**Fig. 1:** Principle scheme of ground water cleaning through stripping and consecutive plasma-catalytic treatment.

facility is shown in Fig. 1. Contaminated ground water is pumped out from the soil, passed and dispersed through the stripper columns. Solved contaminants were dissolved and taken over by the air stream. The cleaned water is returned to the soil, the loaded air flow goes through the catalytic converter, operating at 400... 500 °C.

For plasma-catalytic treatment a partial flow (up to 60 m<sup>3</sup>/h) of the stripper air could be fed into the plasma reactor. The non-thermal plasma results from a barrier discharge and is followed by another catalytic converter at lower temperature (110 °C). The converter was filled with 10 l of Fe-Mn mixed oxide catalyst, resulting in a space velocity of 6000 h<sup>-1</sup> at 60 m<sup>3</sup>/h flow. In order to destroy excessive ozone and to prevent the emission of hydrogen chloride, the catalytic reactor was followed by an 200 l vessel, filled with activated coal.

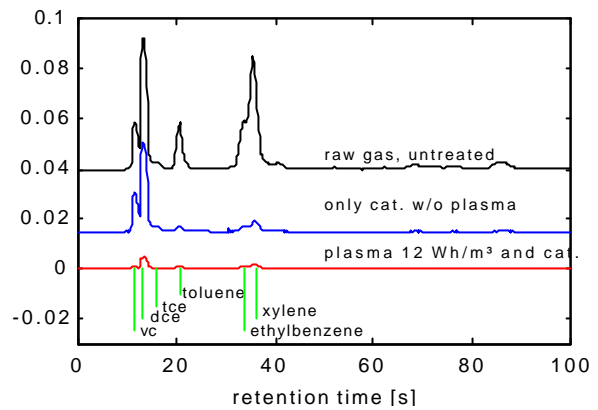
The compact, planar barrier discharge reactor was installed in a special container together with its power supply and the diagnostic equipment. It had a total discharge volume of 3.1 liters. Borofloat glass of 2 mm thickness was used as dielectric barriers in combination with stainless steel plates as electrodes leaving a discharge gap of 2x2 mm. The discharge was operated at 400 Hz sinusoidal voltage at 8-10 kV rms and could deliver up to 1500 W into the plasma.

A photoionisation detector (PID) and a portable process gas chromatograph (GC-PID) with integrated gas pumps were used for on line gas analysis. While the PID measured the integral organic load, the GC-PID monitored the spectrum of the individual organic components. A short multicapillary column and an internal air based gas loop ensured short measuring times (2 min) without the need of a sample gas. Air samples were taken via 6 mm PTFE pipes from the different measuring points: before (raw air) and behind the plasma reactor (plasma treated air) and downstream to the catalytic converter (plasma-catalytic treated air). Before entering the analytic equipment the samples passed through a gas cooling unit in order to minimise the influence of air humidity.

## RESULTS

In accordance with ground water analysis vinyl chloride (VC), cis-dichloroethene (DCE), trichloroethene (TCE), toluene, ethylbenzene and xylene have been found as main components in the stripper air. The absolute amount of these substances as well as their relative concentrations varied considerably from day to day due to the specific working regime of the stripper facility (discontinuous water supply, pumping from different sources). Single component concentrations were in the range from 1-10 ppm.

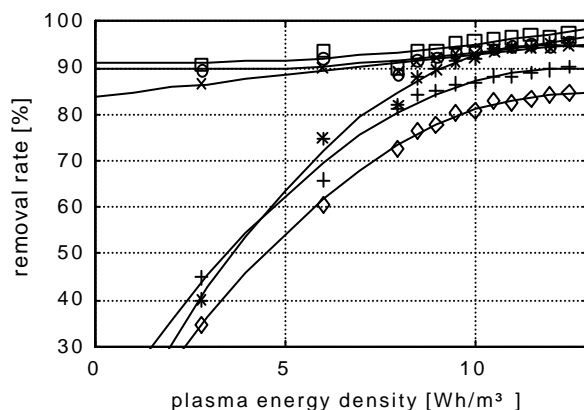
Fig. 2 shows a representative GC spectrum of the raw stripper air together with two spectra taken after pure



**Fig. 2:** GC-spectra of stripper air, from top: untreated raw gas, only catalyst w/o plasma, with plasma and catalyst

catalytic and plasma-catalytic treatment respectively. No by-products could be detected within the measurement limits.

The figure illustrates that at 110 °C catalytic treatment alone is quite different for the six organic components. While aromates show a large reduction the chlorocarbons are only little affected. More clearly this behaviour can be seen in fig 3. Here, in a special run, the removal efficiency (defined as the ratio of measured output to input concentration for a specific component) was determined in dependence on specific plasma energy. At energy densities approaching to zero the aromatic compounds toluene, xylene and ethylbenzene are removed by the catalyst alone to more the 80 %. In combination with plasma treatment the removal rate grows up to more than 95 % at an energy density of 12 Wh/m<sup>3</sup>. On the other side the halocarbons vinyl chloride, dichloroethene and trichloroethene remain nearly unaffected without plasma, whereas preliminary plasma activation with 12 Wh/m<sup>3</sup> increases the corresponding removal rates to values from 85 % (TCE) to 95 % (VC).

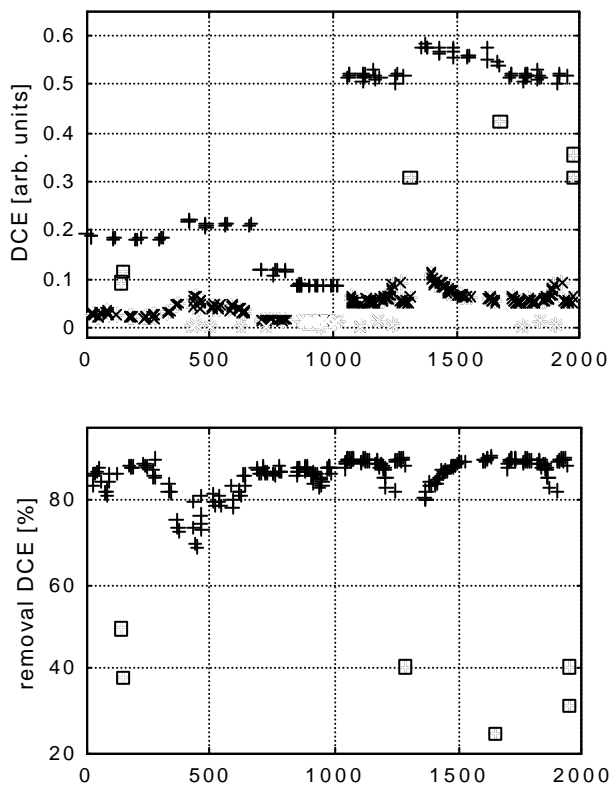


**Fig. 3:** Removal rate for different compounds as function of applied plasma energy density, ★ - VC,

+ DCE,  $\diamond$  - TCE, o - ethylbenzene,  $\square$  - xylene, x - toluene, catalyst at 110 °C

In a long-term experiment the plasma-catalytic system was operated in the stripper facility for more than 40 hours including continuous runs of about 8 hours.

During this time no obvious change in the overall removal rate could be observed. So both the plasma reactor and the catalyst were sufficiently stable against the poisoning halogens and could work at high humidity levels without breakdown or degradation. As an example, Fig. 4 shows this long-term run for cis-DCE. The points in the upper graph represent absolute GC measurements taken sequentially for raw and plasma-catalytically treated air. Squares denote samples from catalytically treated air without plasma. The corresponding calculated removal rate is plotted in the lower graph. Despite of the relatively large changes of input concentrations the observed removal rates remain between 80-90%. So the DCE concentration could be lowered by one order of magnitude, spending about 12 W of plasma power to a flow of 1 m<sup>3</sup>/h. As it was always mentioned this value is equivalent to an adiabatic temperature rise of about 40 K.



**Fig. 4:** Temporal concentration scan of cis-DCE in the stripper air, with and without plasma-catalytic treatment (top) and corresponding calculated removal rate, squares denote catalytic removal alone without

plasma, variations in the removal rate reflect input energy variations from 6-12 Wh/m<sup>3</sup>

In order to understand the plasma-catalytic processes more clearly additional studies under laboratory conditions were carried out [4]. It could be found that

- for a ternary mixture of VC, DCE and benzene (10 ppm each) in dry air the carbon balance is closed, if catalyst temperature is above 100 °C,
- in a mixture of VC and DCE (10 ppm each) in dry air treated by plasma at 14 Wh/m<sup>3</sup> no hazardous substances like PCDD/F, PCB and polycyclic aromatic hydrocarbons are synthesised.

Further studies are necessary to check the different conditions in the field experiment.

## SUMMARY

We have studied the potentials of plasma-catalytic off-gas cleaning in a field experiments at a ground-water cleaning facility, where 60 m<sup>3</sup>/h of contaminated stripper air were treated in a dielectric barrier discharge, followed by a low temperature catalytic reactor at a working temperature of 110 °C. The total organic input concentration was  $\approx$ 100 ppm (C1).

In the complex mixture of chlorinated hydrocarbons and aromates in humid air removal rates of at least 85% for each of the components were obtained.

In agreement with laboratory experiments it could be demonstrated that the combination of non-thermal plasma and low temperature catalysis enhances volatile organic compound removal, generally lowers the content of new reaction by-products and moves the whole process towards more complete oxidation.

Moreover, the dielectric barrier discharge reactor was proofed to work stable under field conditions. It can be easily scaled up to higher volume flows.

## ACKNOWLEDGMENTS

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