Research Articles: Chemical Warefare Agents

Destruction of Diphenylarsine Chloride (CLARK I) with Activated Ozone

[1] **Rainer W. Sieke**, [2] **Günter Lippke**, [2] **Alfred Krippendorf**, [3] **Rainer Haas**, [2] **Sven Lüdtke**

[1] Technologie Consulting GmbH, Echterngrund 19, D-30657 Hannover, Germany
[2] Hazard Control GmbH, Versuchsfeld Trauen, D-29328 Faßberg, Germany
[3] Büro für Altlastenerkundung und Umweltforschung, Stadtwaldstr. 45a, D-35037 Marburg, Germany

Corresponding author: Dipl. Ing. Rainer W. Sieke

Abstract

The new technology of Plasmazon® uses the extremely strong oxidation of radicals to break up the compocunds of organic connections, e.g. chemical warfare agents like Clark I. In making a comparison of oxidation to normal ozone, the factor of the Plasmazon®-technology is available up to 10^3.

The investigation in an experimental test shows that it is possible to destroy the warfare agent character of Clark I. As the possibility of a large-lot application this technology is the method of choice for other chemical or biological warfare agents.
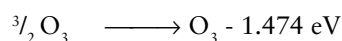
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1 Theoretical Introduction into Activated Ozone Structures

The principle of ozone generation is to generate atomic oxygen (O) in a first step from molecular oxygen (O_2) by dissociation which, in a second step, leads to the formation of ozone (O_3) via a subsequent addition reaction. Allowing for the energies required for reaction, the chemical reactions in the simplest case may be described as follows:

$$O_2 \longrightarrow 2\,O \ - 5.116 \text{ eV}$$

$$O + O_2 \longrightarrow O_3 + 1.084 \text{ eV}$$
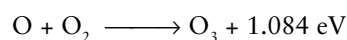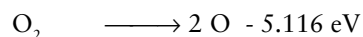
Hence follows the overall reaction:

$$\tfrac{3}{2} O_3 \longrightarrow O_3 - 1.474 \text{ eV}$$

From this, a specific minimum demand for energy of 0.82 kWh/kg is calculated, leading to a maximum theoretical ozone yield of 1,220 g/kWh. Commercially used ozone plants, however, under most favorable conditions achieve only an energy recovery of 14% compared to the theoretically possible ozone yield.

The ozone generators applied so far primarily aimed at the utilization of the ozone, although it was known that ozone is highly toxic and has a half-life of more than 5 hours. Many applications utilize its toxic phase (for the killing of germs and viruses, etc.), other applications the oxidative phase (bleaching processes, industrial oxidation, etc.). Thus, technical improvements mainly aimed at increasing the ozone yield. The underlying problem is that the amount of energy needed is relatively high due to the fact that the major portion of the energy fed into discharge is lost for the ozone synthesis, and finally is converted to heat. Since the use of ozone in a wide range of applications turned out to be uneconomical – due to these losses, the long half-time-values required for obtaining O-radicals which are necessary for the oxidation processes and the subsequent destruction of residual ozone – it is rarely used these days compared to its manifold possible applications.

The major objective of this procedure and the test arrangement is to apply most recent scientific findings and perform the generation of ozone and ozone in its excited state. In the following, the various ozone structures are referred to as "activated ozone structures".
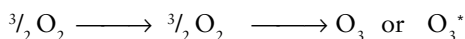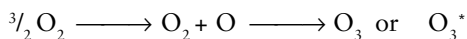
Since 1987, the generation of ozone has been described in detail as two basic reactions:

1. the decay of the molecular oxygen in the basic state $0_2(^3\Sigma^-\text{g})$

2. the activation of molecular oxygen [$O_2\,(^1\Delta\text{g})$, $O_2(^1\Sigma^+\text{g})$, $O_2(^3\Sigma^-\text{g,v})$]

Thereby, the following activated ozone structures may develop:

- basic state
- excited state
- ionized state O_3^+ and O_3^-

Schematically, the above described process may be summarized as below proceeding from the basic state:

$$^3/_2\,O_2 \longrightarrow O_2 + O \longrightarrow O_3 \text{ or } O_3^*$$

$$^3/_2\,O_2 \longrightarrow {}^3/_2\,O_2 \longrightarrow O_3 \text{ or } O_3^*$$

whereby O_3^- represents the activated ozone structures $[O_3(^3B_2)\text{. } O_3(^1A_1,v), O_3(^1B_2)]$, O_3^+ and O_3^-.

The half-time values of these activated ozone structures is said to range between 70 msec and 70 sec, which means that the number of radicals available for oxidation is considerable larger in a shorter period of time.

Activated ozone structures are produced by withdrawing the ozone from the discharge gap as quickly as possible following the dissociation of molecular oxygen (O_2) to atomic oxygen (O) and the subsequent formation of ozone. This impedes the repeated decay resulting from an electron collision in the discharge gap.

The ozone synthesis during an electric discharge basically needs a plasma which is characterized by a high temperature of electrons and a low temperature of gas. With the passage through the gas-permeable electrode, the essential physical conditions for the plasma ensuring optimal reaction phases are met, namely that the electron temperature is higher than the temperature of the ions, atoms and molecules present in the gas.
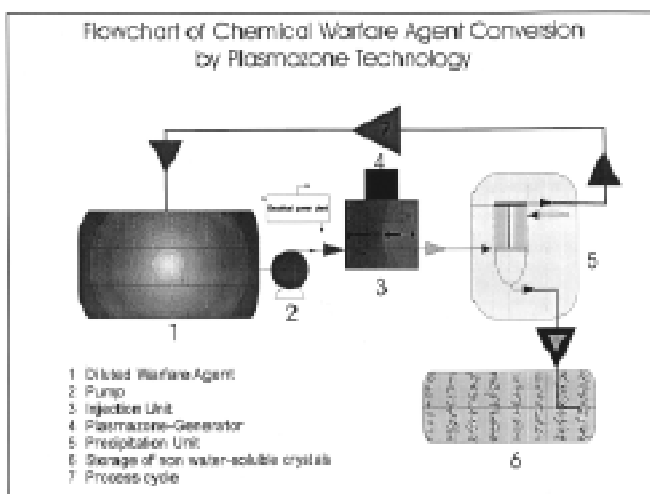

Fig. 1: Flowchart of the Plasmazon-technology

The formation of the activated state $O_3(^3B_2)$, $0_3(^1A_1,v)$ $O_3(^1B_2)$, O_3^+ and O_3^- is also much favored by electrons colliding with the electrode sheathing or the conductive filling material of the electrode, causing an exchange of electrons.

Among the favorable physical conditions for the plasma is also the pressure in the discharge space. It influences the time required for maintaining conditions in a non-thermal plasma in such a manner as to keep the electron temperature above that of the ions, atoms and molecules present in the gas [1-7]. In **Figure 1**, a flowchart of the Plasmazon-technology is shown.

Knowing this an experimental test was performed with a very complicate agent to destroy, the chemical warfare agent diphenylarsine chloride.

2 Experimental

1.4 g diphenylarsine chloride (CAS-No. 712-48-1) was diluted in 50 ml acetone (c = 28 g/l). Through the acetonic solution activated ozone was pressed with a flow rate of 300 ml/min by room temperature. After a reaction time of 1.5 h, a precipitation of white crystals was observed (→ *Fig. 2*). The reaction was stopped after the precipitation ended.

Fig. 2: Precipitation of white crystals, reaction time 1.5 h

The white crystals were filtered. They are not soluble in acetone and water (pH 7), but soluble in diluted sulphuric acid and dichloromethane.

The analysis of a diluted sulphuric acid extract of the crystals shows no As(III). After boiling the crystals with 3 ml 97% sulfuric acid and 1 ml 30% hydrogen peroxide for ten minutes, the analysis shows a concentration of As(III) of 23.5%. The white crystals are an organic arsenic compound.

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Table 1: Destruction of chemical agents

Destruction of Chemical Agents					
Agent in %	after 1st line	after 2nd line	after 3rd line	after 4th line	after 5th line
100%	98%	99.96%	99.9992%	99.99998%	99.999999%

The analysis of As(III) was done photometrically with silver dithiocarbamate [8].

The acetonic solution was analyzed with gas chromatography/mass spectrometry after filtering the white crystals. The following products were identified:

- diphenylarsine chloride (c = 0.56 g/l; reduction rate: 98%)
- trichloro acetic acid ethyl ester
- dichloro acetic acid
- chloro acetone and
- chlorobenzene

3 Discussion

- After treatment with ozone, the quantity of diphenylarsine chloride in the solution was reduced to 2% of the starting concentration. The white crystals are probably high molecular oxidation products with phenyl-arsine structures, although an identification with gas chromatography/mass spectrometry was not possible. The identification of chlorobenzene shows that the phenyl-arsine-bonding was cracked by the Plasmazone process.

- Trichloro acetic acid ethyl ester, dichloro acetic acid and chloro acetone are reaction products of acetone and chlorine from the destruction of diphenylarsine chloride. Chlorobenzene results from the fragmentation of diphenylarsine chloride (chlorine and benzene).

- The settings of the Plasmazon®-generator were on standard. Only one-line effects were tested, no circulation procedure. We took the CLARK I -agent, because it is one of the most difficult chemical warfare agents to oxidize and to destroy. We wanted to show that it is possible to destroy the warfare-character in a mobile, closed test-room and not dangerous manner with the Plasmazon®-technology: We reached a destruction of more than **98%** in only one treatment-turn (→ *Table 1*).

- Beside the special treatment of nerve agents like Sarin, Tabun, Soman, we want to give the idea of the destruction e.g. of VX: The relative high density of electrons on Thiolsulfur furthers the electrophilic attack, e.g. by oxidation. A strong oxidation breaks up the phosphor-sulfur-linkage. We have developed own direct chemical measurement of the nerve toxicity which is controlling the destruction-unit.

The successful tests of oxidation of Clark I (CAS-Nr. 712-48-1) have shown that the treatment of Lewisite or other chemical warfare agents could be the method of choice. The detoxification-reaction of Lewisite can be uprated to an advanced mineralization by the Plasmazone-technology. The circulation-system makes it possible to treat the rest of a line before with the new agents.

In a careful calculation it seems to be possible to handle about 2 tons of agents per day with one conversion-unit. Also, it seems to be possible to upscale a unit up to 10 tons per day.

4 References

[1] EHMER, K.: Patentschrift DE 196 27 509 C 2

[2] SIEKE, R. (1998): Poster Cold Combustion. Poster Symposium Munster-Destruction of Chemical Warfare Agents. Munster, March 1998

[3] VDI-Richtlinie 3891 (1992): Emissionsminderung. VDI – Handbuch Reinhaltung der Luft Bd.3. VDI Düsseldorf, 1992

[4] ADDINK, R.; PAULUS, R.; OLIE, K. (1995): Unterdrückung der Bildung von PCCD und PCDF. Abfallwirtschafts-J. 7, 313-316

[5] VOGG, H. (1995): PCDD/F und Abfallverbrennung. Organohalogen Compounds 22. Dioxin-Informationsveranstaltung, EPA Dioxin Reassessment, Bayreuth, p. 31ff.

[6] SIEKE, R.: Aktivierte Ozonstrukturen. Unpublished

[7] PENETRANTE, B.; SCHULTHEIS, S. (1993): Non-Thermal Plasma Techniques for Pollution Control. NATO ASI Series, Vol. 34, Part A + B. Springer-Verlag, Berlin, Heidelberg

[8] Deutsches Institut für Normung (1968): Bestimmung des Arsen-Ions. DEV D 12