

# SELF-PROPAGATING HIGH-TEMPERATURE DEHALOGENATION

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| <b>Name of Process:</b><br>Dehalogenation by Self-propagating High-temperature Reactions<br>Self-propagating High-temperature Dehalogenation  | <b>Status:</b><br>System has been operating at labscale in Italy.<br>The system does not yet operate commercially. |
| <b>Vendor:</b><br>Centro Studi sulle Reazioni Autopropaganti  |  |
| <b>Applicable Pesticides and related POPs wastes:</b><br>Toxic Chlorinated Aromatics  |  |
| <b>Introduction note:</b><br>As there are hardly any "neutral" documents available on this technology, some of the material has been used in order to give the minimum necessary information on this method. The destruction of health threatening compounds has become an important subject in the area of hazardous waste management. Organo-chlorine pesticides, polychloric biphenyls, dibenzofurans, dioxins and other synthetically produced derivatives of chlorobenzene are some of the most profuse (and politicized) of these substances. Indeed, aromatic rings with halogen substitution are highly resistant to oxidative degradation and the possible emission of even more toxic by-products appears one of the main disadvantages of conventional incinerator technologies.   |  |
| <b>Technology description:</b><br>The technology is based on the exploitation of self-propagating reactions to meet the current "hot topic" of treating chlorinated aromatics. The point is that the reaction of many chlorinated organic compounds with strongly reductive substrates, such as alkaline metals or their hydrides, is very exothermic and thermodynamically quite favorable. Typical reaction enthalpies are well above 1000 kJ per mole. Likewise, the adiabatic temperature of these processes can be extremely high, as high as 4000 K. These features are similar to those currently met in typical processes based on self-propagating reactions where a spontaneous propagation of the reaction takes place in the form of a combustion wave. The consequence is that severe thermochemical conditions, suitable for the breakdown of hazardous organic molecules, can be reached at the self-propagating combustion front.   |  |
| <b>Process diagram:</b><br>The main steps in the process are: <ul style="list-style-type: none"> <li>• LOADING THE GREEN MIXTURE INTO THE REACTOR</li> <li>• SEALING AND IGNITION</li> <li>• REACTION</li> <li>• COOLING</li> <li>• UNSEALING</li> <li>• UNLOADING</li> </ul> Our chlorinated test compounds were hexachlorobenzene and the racemate of 2-(2-4-dichlorophenoxy)-propanoic acid, (C <sub>9</sub> H <sub>2</sub> Cl <sub>2</sub> O <sub>3</sub> ), a commercial herbicide known as Dichlorprop -hereafter 2,4-DP. Calcium hydride, or calcium, was used as a reductive agent. The process we followed is quite simple. Reactants were mixed and pressed into cylindrical pellets and fitted into the sample holder of the reaction chamber. The reaction was run under a slight overpressure of purified argon. Samples were fired by a power pulse (2 s) of about 2 kW by means of a tungsten coil. After the thermal spike the reaction spreads spontaneously through the whole sample. The propagation front through the pellet is clearly discernible leaving behind a zone of burnt powders which scatter away due to an intense evolution of the gaseous products accompanying the combustion process. These features reflect the highly exothermic qualities of the reactions involved. From reference data, a reaction enthalpy of 1709.6 kJ/mole is foreseen for a direct and complete reduction of hexachlorobenzene as: $3CaH_2 + C_6Cl_6 \rightarrow 3CaCl_2 + 6C + 3H_2 \quad (-1709.6 \text{ kJ/mol})$ which rises to 1804.6 kJ/mole when an excess of CaH <sub>2</sub> is employed: $6CaH_2 + C_6Cl_6 \rightarrow 6CaHCl + 6C + 3H_2 \quad (-1804.6 \text{ kJ/mol})$ In the case of 2,4-DP, the following reactions were tentatively assumed: $4CaH_2 + C_9H_8Cl_2O_3 \rightarrow 3CaO + CaCl_2 + 9C + 8H_2 \quad (-1295.4 \text{ kJ/mol})$ $5CaH_2 + C_9H_8Cl_2O_3 \rightarrow 3CaO + 2CaHCl + 9C + 8H_2 \quad (-1321.7 \text{ kJ/mol})$ The resulting reaction heats are large enough to maintain the self-sustaining character of the process within a wide range of compositions. Indeed the combustive regions are similar for the two test compounds, and extend from a CaH <sub>2</sub> /organohalide molar ratio of about 2-3 up to 15-18. The maximum temperature of the propagating reaction front was observed in the stoichiometric ranges given above. For example, a combustion temperature above 2650 K was registered using an infrared pyrometer for a CaH <sub>2</sub> /C <sub>6</sub> Cl <sub>6</sub> mixture with a molar ratio of 3. This value is similar to the calculated adiabatic temperature of 2984 K. The reaction temperature progressively decreased with increasing the CaH <sub>2</sub> content in the mixture. This is due to the excess of CaH <sub>2</sub> which does not contribute to the reaction heat, while increasing the total heat capacity of the system. For example, from self-generating temperature profiles related to a CaH <sub>2</sub> /2,4-DP molar ratio equal to 12 and registered by two thermocouples embedded in the pellet we note that the reaction propagation rate resulted of 0.8 cm/s. This parameter was also obtained from video-records and the reaction propagation rate for the whole range of examined compositions was found to be between 0.5-1.5 cm/s. |  |

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## Performance:

### Treatment efficiency:

There are only a limited number of data available, which have been compiled below.

According to the straightforward pathways proposed above, low  $\text{CaH}_2$ /organohalide benchmark ratios are demanded for the complete reduction of the chloroorganics. At least three moles of calcium hydride are required in the case of hexachlorobenzene and four or five in the case of 2,4-DP. Therefore, in presenting analytical results, we will focus on mixtures containing a stoichiometric excess of  $\text{CaH}_2$ . Samples from the reactor's head space were analyzed by Gas Chromatography/Mass Spectroscopy (GC/MS). Hydrogen and methane (with CO and  $\text{CO}_2$  in the case of 2,4-DP) were the main gaseous compounds. Traces of benzene, mono-, di- and tri-chlorobenzene, dichloroethylene, dichloro-methane, xylene and trimethylbenzene were also found by utilizing EPA Method TO15. Organic solid end-products in the reacted powders were also analyzed by high resolution GC/MS. We found consistent concentrations of reaction products, the total organo-chlorine conversion resulting in each trial greater than 99.999%.

As shown in the following Figure, the conversion of the reactants to non-toxic end-products and the transformation routes were also confirmed by the X-ray analysis. In the case of hexachlorobenzene, the burnt powders were seen to consist of graphite,  $\text{CaCl}_2$  and  $\text{CaHCl}$ , the hydride-chloride mixed salt becoming the predominant phase at the larger  $\text{CaH}_2$  content. In the case of 2,4-DP  $\text{CaO}$  was also found.

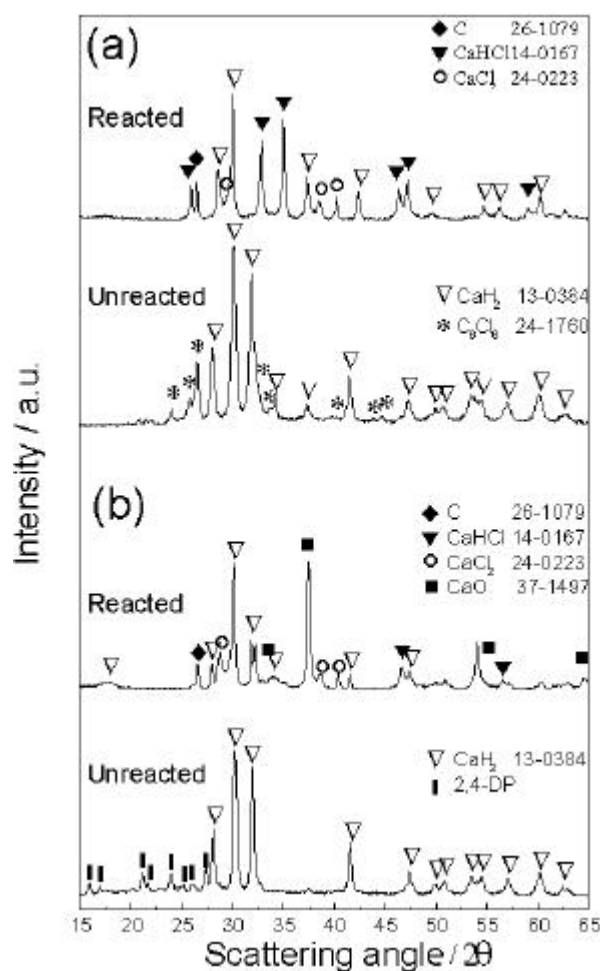


Figure Caption.  $\text{CuK } \alpha$  XRD patterns of the burnt powders for (a)  $\text{CaH}_2$ - $\text{C}_6\text{Cl}_6$  mixture with a molar ratio of 12 and (b)  $\text{CaH}_2$ -2,4-DP, with molar ratio of 12. The patterns of the as-prepared mixtures are also reported. The angular positions of the main peaks are shown according to the JCPDS file quoted in the inset. Notice the formation of  $\text{CaO}$  in the case of 2,4-DP.

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| <p><b>Throughput:</b><br/>no data available!</p>  |
| <p><b>Wastes/Residuals:</b><br/>see data mentioned before</p>   |
| <p><b>Reliability:</b><br/>Successful tests were carried out with other chlorinated compounds and also using different substrates. In particular, it is interesting to note that the use of metallic calcium increases the reaction heat for the hexachlorobenzene reaction up to - 2243 kJ/mole with a <math>T_{ad}</math> of 4041 K, thereby creating still more effective reduction conditions.</p>  |
| <p><b>Limitations:</b><br/>To be investigated</p>   |
| <p><b>Transportability:</b><br/>To be investigated</p>  |
| <p><b>Detailed information:</b><br/>No Annex</p>  |
| <p><b>Full Scale Treatment examples:</b><br/>No data available!</p>   |
| <p><b>Conclusion:</b><br/>These results suggest that self-activating processes can be an alternative to conventional thermal treatments of hazardous chlorinated aromatics. The advantages are obvious in that very high temperatures are locally reached with low pressure and under extent-controlled conditions. Solid and gaseous reaction products can be easily checked before their discharge. The simplicity and a very low energy requirement are two other merits of the process.</p> <p>The system has only been operating at lab scale, the following phases of pilot tests have to be performed and the various independent assessments have to be made. The system does not yet operate commercially.</p> |
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| <p><i>*Note: This NATO/CCMS fellowship report does not certify any particular technology, but tries to summarise the state of the art of the concerned technology on the basis of data delivered by the company or other source, which have been made available to the author and refers the reader to original documents for further evaluation. Without the efforts of the Technology supplier it would not have been possible to set up this fact sheet.</i></p> <p><i>** Note: The text for this report is verified by the Technology supplier on 12. December 2002</i></p>   |

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## **References:**

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## ***Self-propagating High-temperature Dehalogenation –Annex to Pesticides Treatment Technology Fact Sheet***

Figure 1: Combustion wave temperature for a  $\text{CaH}_2/2,4\text{-DP}$  sample with a molar ratio of 12. Traces were registered with two thermocouples inserted 1 cm apart along the pellet axis. The time shift at the onset of the rising edges allows one to determine the propagation rate of the reaction front.

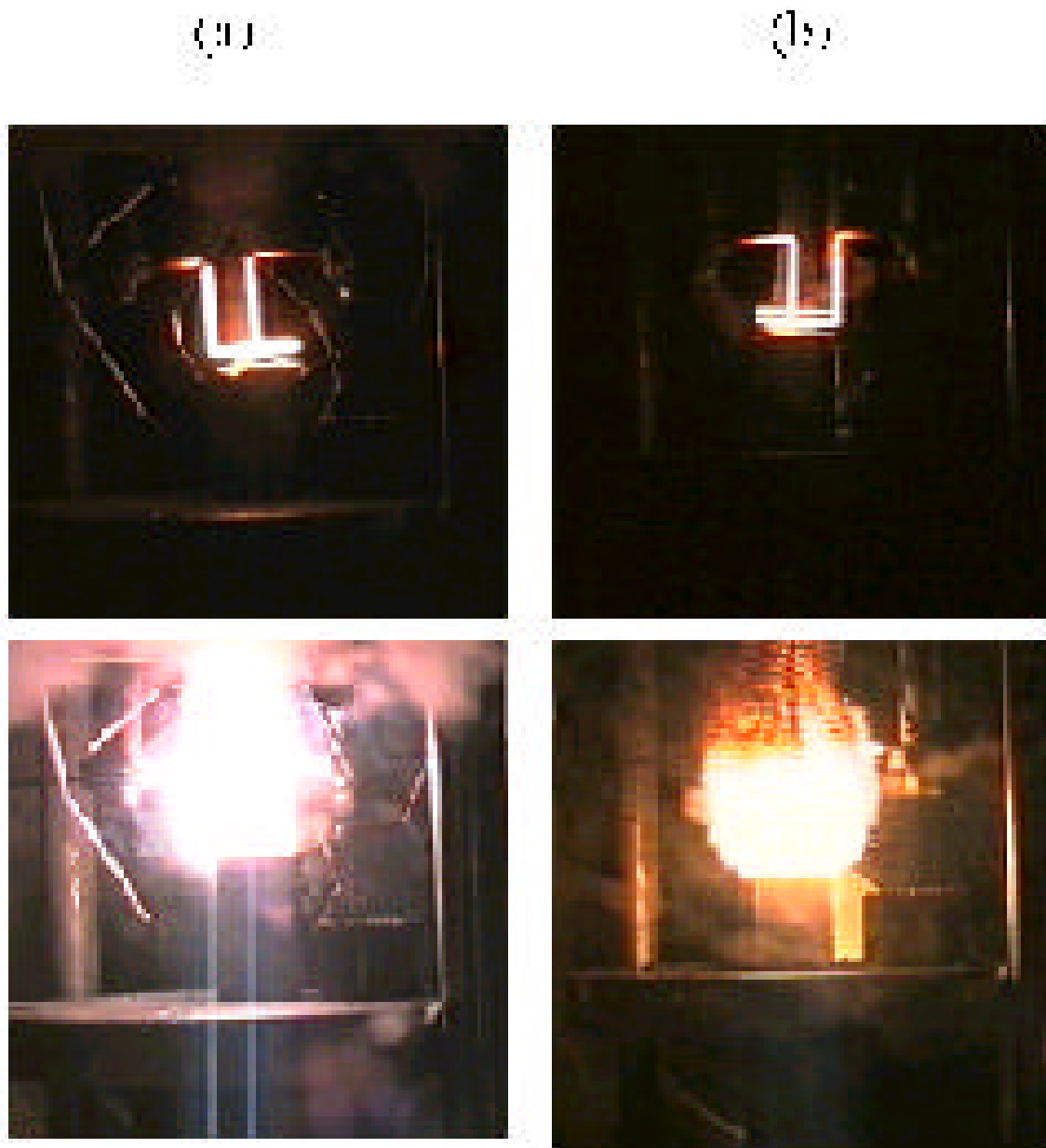


Figure 1