COPPER MEDIATED DESTRUCTION (CMD) – A NOVEL BAT TECHNOLOGY FOR POPs DESTRUCTION

Ocelka T[1]., Pekárek V[1]., Fišerová E[2]., Abbrent M[1]., Kohutová J[1]., Hetflejš J[2]., Lojkásek M[1].

[1] Institute of Public Health Ostrava, Partyzánské nám. 7, 702 00 Ostrava, Czech Republic, Tomas.Ocelka@zuova.cz
[2] Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, v.v.i., Rozvojová 2, 165 02 Prague 6, Czech Republic

Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs) defines as one of its aims the application of technologies to minimize environmental threats posed by POPs. In Article 6 of the convention there are performance standards stated for the use of best available technologies (BAT) to dispose of stockpiles of PCBs and other POPs. The top priority is set for the irreversible and technically feasible destruction of POPs. Incineration processes have recently been used, but the present interest focuses on non-combustion technologies. In order to evaluate technologies some important principles were outlined[1], with the main objective to minimize the formation and emission of POPs, mainly PCDD/Fs.

A novel non-combustion technology called Copper Mediated Destruction (CMD) was recently developed and patented[2]. The principles, experimental parameter and trial experiments of the copper mediated destruction method (CMD) were recently presented[3-6] for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), organochlorinated pesticides (OCPs, like DDTs and metabolites, x-HCHs, PCPh, PCBz, etc.…).

Some new results are presented in this work as part of the introduction to the full-scale unit, in a mobile arrangement for broad applications.

Materials and Methods

As an experimental set-up for remediation, testing was established in following reaction systems:

- Laboratory small-scaled reactor,
- Laboratory full-scaled reactor,
- Semi-scaled reactor.

Results were used for optimization of the CMD full-scale unit.

All the tests were carried out on principles mainly given by developed and patented procedures[1].

Sampling, analysis

All sampling and testing methods were validated (accredited) according to the ISO 17025 standard. An isotopic dilution method using ^{13}C-labled compounds was used for the final analysis of OCPs. Analysis was carried out on the GC-MS/MS system (Finnigan); for preliminary screening the ECD method was used.

Dehalogenation experiments

Testing was conducted on real contaminated samples of the following loads:

- Area marked as “Klatovy” – residuals of pesticides after use in local agriculture (relatively low levels).
- Area marked as “Jaworzno” – mixtures of various pesticides from their recent production taken in from Central landfill (high level of contamination).

All experiments were performed in non-optimised regimes, after homogenization, without any special matrix treatment or contaminant isolations (e.g. by thermal desorption unit).

Results and Discussion

Compilation of results is given in Table 1.

B.D. – concentration before destruction, A.D. – concentration after destruction

Areas: Jaw = Jaworzno, Kl = Klatovy

BDL = below detection limit

NA = not detected (not relevant) for the site

		B.D.	A.D.	B.D.	A.D.	B.D.	A.D.	B.D.	A.D.
Sample №		**Jaw 5219**	**Jaw 5223**	**Jaw 13518**	**Jaw 19937**	**Kl 23171**	**Kl 26330**	**Kl 23172**	**Kl 26331**
alfa-HCH	mg/kg	4700	<0.5	58000	1.3	<0.5	<0.5	3.6	<0.5
beta-HCH	mg/kg	760	<0.5	9700	<0.5	1.9	<0.5	<0.5	<0.5
gama-HCH	mg/kg	900	<0.5	370	<0.5	10	<0.5	380	<0.5
delta-HCH	mg/kg	330	<0.5	230	<0.5	<0.5	<0.5	0.53	<0.5
Σ	**mg/kg**	**6690**	**BDL**	**68300**	**1.3**	**12**	**BDL**	**384**	**BDL**
HCB	mg/kg	11	<0.5	12	0.63	<0.5	<0.5	<0.5	<0.5
o,p-DDD	mg/kg	140	<0.5	4.8	<0.5	5.3	<0.5	260	<0.5
o,p-DDE	mg/kg	5.8	<0.5	<0.5	<0.5	<0.5	<0.5	35	<0.5
o,p-DDT	mg/kg	30	<0.5	7.9	<0.5	14	<0.5	540	<0.5
p,p-DDD	mg/kg	460	<0.5	25	<0.5	14	<0.5	650	<0.5
p,p-DDE	mg/kg	25	<0.5	4.3	<0.5	6.8	<0.5	660	<0.5
p,p-DDT	mg/kg	66	<0.5	260	<0.5	42	<0.5	1200	<0.5
tetradifon	mg/kg	NA	NA	30	<0.5	NA	NA	NA	NA
dinoseb	mg/kg	NA	NA	NA	NA	20	<1	3.4	<1
Σ	**mg/kg**	**726.8**	**BDL**	**344**	**BDL**	**102**	**BDL**	**3348**	**BDL**

Table 1 Results from CMD destruction of some contaminated samples

Conclusions

The analyses show that both hexachlorocyclohexane isomers (HCH) and dichlorodiphenyl derivatives (DDD, DDE, and DDT), are efficiently destroyed by the detoxification method CMD. The destruction below detection limits is also achieved for a wide range of initial HCHs concentrations. The same is also true for hexachlorobenzene (HCBs) and specific pesticides such as tetradifon and dinoseb.

In summary all the samples were efficiently dehalogenated. This provides strong support for a possible scaling-up of this method, to be applicable for (based on a large series of experiments performed outside this paper):

- contaminated soil,
- highly contaminated fly ash from catalytic filters of waste combustion units,
- toxic waste from filters and gas absorbents (activated carbon, heaven-dust),
- other toxic deposits,
- liquid and solid wastes containing PCB, biocides, or other POP substances,
- concentrated absorbing fillings,
- construction materials,
- carbonic filter media,
- cleansing sands,
- liquid material (waste oils) on suitable carriers.

Acknowledgements

This work was supported by the Ministry of Industry and Trade of the Czech Republic - Project IMPULS (FI-IM5/253) and Central Europe, under project acronym FOKS (1CE026P3), which are kindly acknowledged.

References

1. Weber, R., *Chemosphere*, 2007, **67**, S109-S117.
2. *United States Pat.*, 20070021639, 2007.
3. Grabic, R., Pekarek, V., Ullrich, J., et al., *Chemosphere*, 2002, **49**, 691-696.
4. Pekarek, V., Grabic, R., Marklund, S., et al., *Chemosphere*, 2001, **43**, 777-782.
5. Pekarek, V., Weber, R., Grabic, R., et al., *Chemosphere*, 2007, **68**, 51-61.
6. Stach, J., Pekárek, V., Grabic, R., et al., *Chemosphere*, 2000, **41**, 1881-1887.