Mechanochemical Dehalogenation

Name of Process: Mechanochemical Dehalogenation (MCD)	Status:
Vendor: Tribochem Website: http://www.tribochem.com Environmental Decontamination Ltd	System has been operating at pilot labscale in Australia, Germany, Norway and New Zealand. The system does not yet operate commercially, but in New Zealand, a full scale remediation is planned, using the MCD process, during 2003 at the FCC site in Mapua.
Applicable Pesticides and related POPs wastes: HCH, DDT, PCB's	

Introduction note:

As there are hardly any "neutral" documents available on this technology, some of the vendors/researchers materials have been used in order to give the minimum necessary information on this method. The author regrets, that after various requests, the vendors/developers were not yet willing/able to provide the necessary information in order to better validate this interesting technology.

Technology description:

Mechanochemistry, using mechanical energy to initiate chemical reactions, is an emerging technology in the field of waste disposal. High energy input is needed, necessitating the use vibratory or planetary balls mills. While some heat is produced during milling, reactions often differ from those initiated thermally. Mechanochemical reactions occur through a number of mechanisms. In a ball mill intense mixing takes place and reactants are brought into intimate contact with each other. Grinding reduces the particle size and increases the surface area available for reaction. New reactive surfaces are exposed during particle fracture and the introduction of dislocations increases the surface reactivity. At the point of contact between two grinding balls during a collision event, a highly localised triboplasma is formed giving energy for chemical reactions to occur. Milling also tends to create radicals, which can then go on to react with neighbouring compounds [1]. All these effects combine to make mechanochemical reactions possible.

In the early 1990s, researchers at the University of Western Australia (UWA) discovered that DDT could be destroyed by milling with calcium oxide [2]. After 12 hours of milling no organic materials could be detected by GCMS. Most of the chlorine reacts with calcium to form calcium chloride and the carbon forms a black graphitic residue containing the remainder of the chlorine. The general equation below was put forward as a summary of the reaction taking place [3]. This is, by the authors own admission, rather simplistic and the detailed chemistry taking place is far more complex [4].

$$2C_{14}H_9Cl_5 + 5CaO \rightarrow C_{28}H_8 + 5CaCl_2 + 5H_2O$$

While the destruction of DDT and other organic chemicals by milling with calcium oxide was successful, long milling times were required. This was deemed to make it uneconomical on an industrial scale and the focus at UWA shifted elsewhere.

Environment Australia has stated in 1997 the following [5]:

While still very much at an experimental stage, the ball milling process has a number of potential advantages :

- the low energy potential of the system in relation to the surrounding environment means that the potential for release of contaminants is reduced. Also, the process can be readily shutdown in a short period of time, further reducing the potential for release in case of an emergency or power failure;
- the process operates at low temperatures increasing safety, reducing energy consumption and reducing the potential for formation of dioxins;
- items of electrical equipment, contaminated with PCB or damaged or corroded waste containers may be fed directly into the ball mill system for destruction;
- the process largely uses well established mineral processing equipment and principles;
- the process by its nature will result in a high degree of mixing of wastes and would tend to break up agglomerated material;
- no gaseous emissions are produced;

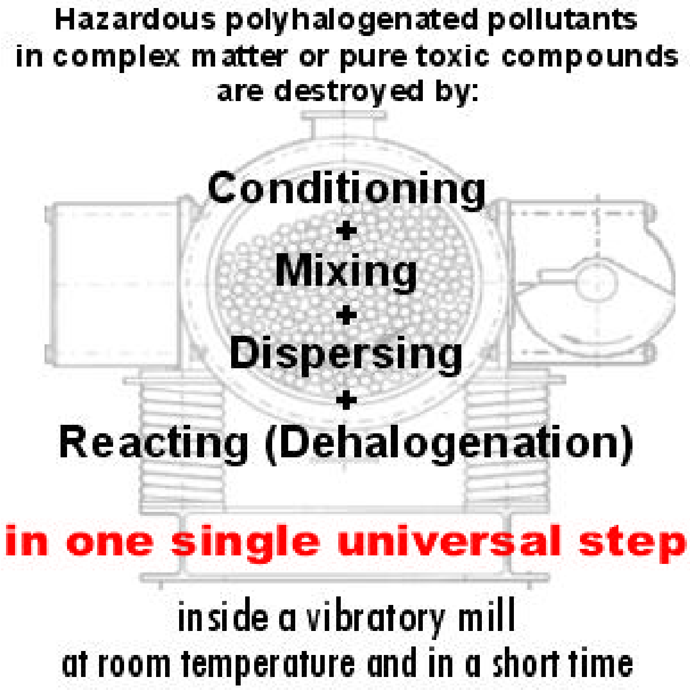
The process is likely to readily treat wastes containing a range of organic contaminants, or mixtures of organic contaminants in one step, reducing waste handling and the associated risk.

John Vijgen, International HCH and Pesticides Association, Fellowship report: "New and emerging techniques for the destruction and treatment of pesticides wastes and contaminated soils." NATO/CCMS Pilot Study: Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)"

Process diagram:

$R\text{–}Cl$	+	Mg	+	"H"	⇒	$R\text{–}H$	+	$MgCl_2$
(PCB)		*Base Metal (Magnesium)*		*Hydrogen-Donor*		*Biphenyl*		*Salt*
TOXIC					⇒	**HARMLESS**		

Figure 1 and 2: Overview of the DMCR process characterization: One example outlined (rough, simplified scheme, not stoichiometric) for dehalogenation using DMCR: PCBs are dehalogenated by Magnesium metal in the presence of an appropriate hydrogen donor (alcohols, polyethers, amines and so forth) yielding harmless biphenyl and magnesium chloride [6].



Performance:

Treatment efficiency:
1. Tribochem
There are only a limited number of data available, which have been compiled below.
Promising laboratory tests on PCB have been executed by Tribochem [7]. These results are shown in the following Table:

Table: Dechlorination of appr. 7,000 ppm PCB (Chlophen A 30) in sand deploying magnesium, methanol and triglyme by means of using a centrifugal ball mill “Retsch S 1” (according to GC MS analyses, external standard).

Mg (eq.)[a]	23	16	12	12	12
î Mg/soil, î RgTot/soil [a]	4.6, 10.3 %	3.4, 9.0 %	2.3, 7.9 %	2.3, 7.9 %	1.1, 6.8 %
time [hr]	5	5	5	7.5	5
Dechlorination (according to GC-MS)	complete °)	complete °)	modest [2])	significant [2])	poor
X(PCB) [%][3])	97.2 [100][1])	97.1 [100] [1])	28.4	49.9	20.2
A(Biph) [%])	78.6	75.2	3.1	7.4	1.8

[a] Magnesium equivalents related to total organic chlorine (Chlophen A 30 = 42 % chlorine content (w/w)),
î = ratio magnesium/(sand + PCBs ("soil")) (w/w), and reagents in total (RgTot)/(sand + PCBs) (w/w).
° Dominating final product: biphenyl; traces: phenylcyclohexane, halogen-free dimethyl-biphenyls, quarter-phenyls, see also Figure 2.
[2] Main (intermediary) products: partly dechlorinated PCB congeners (two monochlorobiphenyls).
[3] PCB degradation (turnover).
[1] First value: reduction of peak area related to total peak area of PCBs prior to degradation (external standard). Second value (in brackets): in the retention range, where PCBs had entirely vanished, traces of entirely dechlorinated compounds were found, therefore a total degradation/dehalogenation is verified.
Biphenyl yield.

Tribochem has also been executing pilot tests in Norway in 1995 and 1996 for PCB contaminated soil stating [11]:

1995: Feasibility study, benchscale, regarding PCB contaminated soil stemming from a contaminated site at a transformer station at Oslo, Norway.
1996: Pilot project, semi-technical scale, directly at the site at Oslo. It was proven that the PCB contaminated soil, coming out of a washing process as a sludge, could be detoxified efficiently and the results met the requirements of the Norwegian legislation and the Norwegian authorities.
In addition, DDT contaminated soil stemming from another Norwegian site could be treated successfully.

Norway 2001 - ongoing: DECONTERRA AS, Horten, Norway, and TRIBOCHEM, Wunstorf, Germany, are currently conducting joint pilot projects for the decontamination of PCB contaminated materials. One focus is on soil fractions stemming from soil washing processes contaminated by PCBs.

Germany 1999:
TRIBOCHEM implemented a joint pilot project with a refinery in Germany. Used lubricating oils contaminated by a considerable number of different polyhalogenated pollutants (aliphatic and aromatic compounds) could be decontaminated efficiently. It was verified that the decontaminated oil could be recycled by conventional distillation and, therefore, had not to be incinerated any longer. The DMCR dehalogenation step can be readily integrated into the entire oil work-up process, requiring only a few adaptions pertaining to the common refinery process for recycling lubricating oils.

However, on the abovementioned projects, Tribochem was not able to disclose more detailed information at the present stage.

2. Environmental Decontamination Ltd (EDL)
Environmental Decontamination Ltd (EDL) of Auckland in New Zealand has developed the MechanoChemical Dehalogenation (MCD) process. Process details and reactants are commercially sensitive and are not divulged here.

Mapua, a pristine spot in New Zealand, at the top of the South Island, is the location where a former pesticide factory used to be. Here DDT concentrations reach more than 3500ppm in some places, far in excess of acceptable levels for residential (5ppm) and commercial (200ppm) use. Dieldrin and aldrin are also present in concentrations over their respective acceptable limits [8].

EDL's MCD process competed with other technologies was shortlisted, trialled and awarded the task of treating the Mapua site. The commercialisation of the process is underway to achieve the target mass destruction of DDX to < 200ppm and Dieldrin+Aldrin+ 10% Lindane to < 60ppm. EDL intends to publish results in the next 12 months [9].

Throughput:
no data available

Wastes/Residuals: By-products of the destruction of organochlorine compounds using CaO are generally of low toxicity and may include graphite, calcium, chloride, [10].

Reliability:
no data available

Limitations:
no data available

Transportability:
not applicable yet

Detailed information:
No Annex

Full Scale Treatment examples:

John Vijgen, International HCH and Pesticides Association, Fellowship report: "New and emerging techniques for the destruction and treatment of pesticides wastes and contaminated soils." NATO/CCMS Pilot Study: Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)"

Conclusion:
Ball milling is a highly interesting technology with a lot of potential for the future for the treatment of pesticides, however it will probably take some years before the technology is full scale applicable and sufficient experiences have been gained. The 2 technology suppliers were only able to deliver very limited information on treatment, thus making a proper assessment not possible. Independent assessments are needed to evaluate this technology in the future.

Environmental Decontamination Ltd (EDL)
Mr. Bryan Black
PO Box 58-609
Greenmount
Auckland
New Zealand
Ph: +64 9 274 9862
Fax: +64 9 274 7393
Email: bryan@manco.co.nz

Tribochem
Mr. Volker Birke
Georgstrasse 14
D-31515 Wunstdorf
Germany
Ph: +49 50 31 6 73 93
Fax: +49 5031 88 07
Email: birke@tribochem.com

**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 deliver by the company or other sources been made available to the author and refers the reader to original documents for further evaluation.*

References:

1. G Heineke, 1984, *Tribochemistry*, Berlin, Carl Hanser Publishing.
2. Rowlands, et al., 1994, *Destruction of toxic materials,* Nature, 367(6460), p. 223.
3. A Hall, et al., 1996, *Mechanochemical reactions of DDT with calcium oxide,* Environmental Science and Engineering, 30(12), pp. 3401-7.
4. R Hart, 2000, *Mechanochemistry of chlorinated aromatic compounds* , PhD Thesis, Department of Chemistry, University of Western Australia, Perth
5. CMPS&F - Environment Australia**,** Appropriate Technologies for the Treatment of Scheduled Wastes**,** Review Report Number 4 - November 1997
6. Economic and ecologically favourable destruction of polyhalogenated pollutants using the DCMR* - technology, Volker Birke, Tribochem, Forum Book, 6th International HCH And Pesticides Forum, 20-22 March 2021, Poznan, Poland
7. Reductive Dehalogenation of Recalcitrant Polyhalogenated Pollutants Using Ball Milling, Volker Birke, University of Applied Sciences North-East Lower Saxony, Suderburg, Germany, The Third Conference on “Remediation of Polychlorinated and Recalcitrant Compounds”, Monterey, May 20-24th 2002
8. J Easton, 2001, *3052 Final Report: Treatment Trials for Organochlorine Contaminated Soil*.
9. Tristan Bellingham, written comments for Pesticides Treatment Technology Fact Sheet, 29 October 2002
10. HCB Environmental Impact Statement, Alternative Technologies Assessment Section 4, URS Australia, Pty Ltd, 17 July 2001
11. http://www.tribochem.de/projects/1996/index.html (December 2002)

John Vijgen, International HCH and Pesticides Association, Fellowship report: “New and emerging techniques for the destruction and treatment of pesticides wastes and contaminated soils.” NATO/CCMS Pilot Study: Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)”