MECHANOCHEMISTRY AND MECHANICAL ALLOYING 2003

JOURNAL OF MATERIALS SCIENCE **39** (2004) 5111–5116

Mechanochemical reductive dehalogenation of hazardous polyhalogenated contaminants

V. BIRKE*, J. MATTIK, D. RUNNE
University of Applied Sciences, NE Lower Saxony, Suderburg, Germany;
Department of Civil Engineering (Water and Environmental Management),
Steinweg 4, D-30989 Gehrden, Germany
E-mail: birke@fhnon.de

Ball mills are utilized as mechanochemical (MC) dehalogenation reactors for defined reductive dehalogenations of various hazardous polyhalogenated pollutants such as polychlorinated biphenyls (PCBs) or pentachlorophenol (PCP) to their parent hydrocarbons in high yields, i.e., biphenyl and phenol, respectively. This versatile technique, designated as "Dehalogenation By Mechanochemical Reaction" (DMCR), can be preferentially deployed for novel approaches regarding hazardous waste management and destruction: contaminated materials as well as highly concentrated or pure contaminants and their mixtures are treatable at room temperature in a short time, virtually regardless of their state. For instance, PCBs in contaminated soils, filter dusts, transformer oils, or as pure substances are dechlorinated to harmless chloride and their parent hydrocarbon biphenyl by applying magnesium, aluminum or sodium metal plus a low acidic hydrogen source (ether, alcohol, amine etc.). DMCR offers several economic and ecological benefits: ball milling requires a low energy input only. Because of the strikingly benign reaction conditions, toxic compounds can be converted to defined and usable products. Furthermore, detoxified materials like transformer oils can be readily recycled, and DMCR facilitates the re-use of scrap metals. No harmful emissions to the environment have to be expected. This paper presents selected results of basic laboratory studies demonstrating the versatility, efficiency and limits of DMCR.

1. Introduction

Recently, it was shown that polyhalogenated pollutants (PCBs, pesticides such as hexachlorocyclohexane (HCH, lindane) or 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) as well as chemical warfare agents) can be destroyed by MC reactions. This opened up the development of novel, innovative *ex situ* remediation and decontamination processes [1–10]. MC degradation can be easily performed using *ball mills* that are readily available in different sizes (treatment of materials up to several tons is possible) and constructions. The pollutants are eliminated directly inside a contaminated material, virtually regardless of how complex its structure may be and how strongly the pollutants may be bound adsorptively to particular compounds (e.g., clays regarding soils). Usually, MC degradation can be performed at low temperatures, i.e., room temperature. Inside the material to be milled, however, very high temperatures may occur, up to several thousand degrees Celsius at points of action in the sub-microscopic deformation zone, where a grain collides at high velocity with a solid surface (quasi-adiabatic energy accumulation, so-called "tribo-plasma" [11]).

However, none of today's known MC approaches for the destruction of hazardous polyhalogenated pollutants has been scaled up to an industrial scope or even commercialized, most probably due to two major reasons. First, some approaches generate/leave numerous intermediates and degradation products, still partly halogenated, associated with an unknown, but evidently potential toxicological risk, e.g., during milling of DDT with calcium oxide [2–4]. For others, actual degradation products have not been identified at all yet. Second, reaction times predominantly range between several hours or even days, therefore revealing a considerable disadvantage compared to common, well-established *ex situ* destruction techniques like incineration. However, a recently developed approach using certain ternary hydrides may be promising regarding scaling up for several fields of application [1].

Here, the novel DMCR approach for the destruction of recalcitrant polyhalogenated compounds such as PCBs or dichlorobenzene (DCB) is reported, using simple and readily available reagents, supplying defined degradation products and showing the potential to afford reaction times in the range of minutes to only a few hours. Reductive dechlorinations of

---

*Author to whom all correspondence should be addressed.

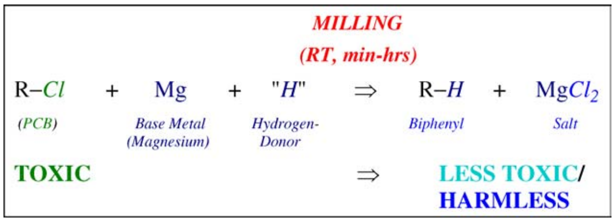

Figure 1 Overview of the DMCR method. One example outlined (rough, simplified scheme, not stoichiometric): during ball milling, PCBs are reductively dechlorinated by magnesium metal in the presence of appropriate hydrogen donors (alcohols, ethers, amines, and so forth) at room temperature yielding biphenyl and magnesium chloride.

polychlorinated *aromatic* compounds are considered, because these compounds are especially recalcitrant, furthermore some of them represent prominent persistent organic pollutants (POPs). For that purpose, base metals like alkali and alkaline-earth metals, but also aluminum, zinc and iron, can be deployed in combination with certain hydrogen donors like alcohols, ethers, amines, and so forth. Fig. 1 outlines the general DMCR approach for PCBs dehalogenated by magnesium metal in a ball mill, as one of numerous combinations possible.

According to Fig. 1, examples of basic MC reductive dechlorinations of PCBs, 1,3-DCB and PCP by milling with magnesium are discussed, which have been part of various laboratory studies and pilot projects covering contaminated soils, oils, fly ashes and solid or liquid waste. Evidently, DMCR treatment can be successfully applied to concentrations spanning from ng/kg up to even pure contaminants [10].

2. Materials and methods

Centrifugal ball mills ("Retsch S 1" and "Retsch S 1000", supplier "F. Kurt Retsch GmbH & Co. KG", Haan, Germany), each equipped with a 50 ml steel grinding jar (containing three steel balls, diameter 2 cm), were used for bench-scale treatability studies.

2.1. Dechlorination of PCBs

The 50 ml steel grinding jar was charged with sand, a mixture of calcium oxide and calcium hydroxide, and triethylene glycol dimethyl ether (triglyme). Pure Chlophen A 30 (a former PCB brand of BAYER GROUP, Germany, representing a technical PCB mixture containing 42% chlorine (w/w), which equals approximately to a trichlorobiphenyl congener) was added, and the materials were blended by grinding for one minute. Afterwards, the jar was loaded with methanol and magnesium (amounts see Table I). The milling process was started and maintained for the required reaction time at about 530 rpm ("Retsch S 1" or "Retsch S 1000"). After that, the finely powdered mixture was extracted with n-hexane for 20 h employing a Soxhlet extractor (prior to the extraction it was carefully mixed with methanol in order to destroy excessive magnesium metal). It was verified that during work-up no additional dechlorination had occurred. The n-hexane phase was washed with water and nitric acid. Then, its volume was reduced to a few milliliters by carefully evaporating at ambient pressure in a Kuderna-Danish-Evaporator. After having cleaned up the reduced n-hexane volume over a small silica gel column and adjusted it to a defined volume, an aliquot part was injected to a GC MS line (Hewlett Packard, model 5972, split/splitless injector, injection according to Grob's method, i.e., splitless during the first 1.5 min, afterwards with opened split (1:23), "HP-5" column (phenyl-methylsilicon), length 30 m, carrier gas: helium; program 1 min. isothermal at 40°C, ramp 15°C/min. up to 280°C).

2.2. Dechlorination of PCP

The 50 ml steel grinding jar was loaded with 15 g of sand containing appr. 4,300 ppm PCP (appr. 99% pure, Merck), 0.76–1.5 g magnesium filings and 0.32–0.64 ml ethylenediamine. The milling process was started and maintained for 30 min at about 530 rpm. After that, an aliquot of 6 g of the finely powdered mixture was transferred into a flask and mixed with 15 ml water and 10 ml 6 N hydrochloric acid while cooling with ice. 10 ml methyl-tert.-butylether (MTBE) were added and the mixture was heated to reflux under vigorous stirring for 30 min. Afterwards, the organic phase was separated, cleaned by centrifugalizing and filtering and dryed (over sodium sulfate). An aliquot part was injected to a GC FID line.

TABLE I Dechlorination of appr. 7,000 ppm PCB (Chlophen A 30) in sand by milling with magnesium and methanol/triglyme in a centrifugal ball mill "Retsch S 1" (according to GC MS analyses, external standard method)

Mg (Equation)[a]	23	16	12	12	5
$\xi_{\mathrm{Mg/soil}}$, $\xi_{\mathrm{RgTot/soil}}$[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[b]	Complete[b]	Modest[c]	Significant[c]	Poor
PCB turnover (%)	97.2 (100)[d]	97.1 (100)[d]	28.4	49.9	20.2
Biphenyl yield (%)	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)), ξ = ratio magnesium/(sand + PCBs ("soil")) (w/w), and reagents in total (RgTot)/(sand + PCBs) (w/w).

[b] Dominating final product: biphenyl; traces: phenylcyclohexane, halogen-free dimethyl-biphenyls, quaterphenyls; see also Fig. 2.

[c] Main (intermediary) products: partly dechlorinated PCB congeners (two monochlorobiphenyls).

[d] 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 PCB degradation/dechlorination is verified (see also Fig. 2).

2.3. Time-dependent, isothermal dechlorination of 1,3-DCB in a sand slurry

The 50 ml steel grinding jar was loaded with 10 g sand, 1.5 g magnesium filings and 15 ml of a mixture of DCB and *n*-butylamine dissolved in cyclohexane (0.0389 ml DCB, 0.5 ml *n*-butylamine). The mill ("Retsch S 1000") was operated for the required time isothermally at the required temperature by deploying an appropriate external cooling/heating jacket (coolant/heating liquid: water), fitting tightly to the steel grinding jar. After ceasing the milling process, the slurry was immediately removed from the jar and filtered. 3 ml of the resulting liquid was treated with acidified water and washed with 10 ml *n*-hexane in a separation funnel. The organic phase was dried over sodium sulfate and afterwards adjusted to a defined volume by adding *n*-hexane. A small aliquot was injected into a GC FID line. To get reliable data, for each data point the described procedure was entirely repeated from the start and was conducted in another, identical 50 ml steel grinding jar, too. The majority of the experiments was conducted in duplicate or triplicate for each given/selected data point, i.e., time value.

3. Results and discussions

3.1. Dechlorination of PCBs during milling with magnesium and alcohols

According to Table I and the corresponding Fig. 2, reductive dechlorinations of PCBs to biphenyl occur during ball milling at *room temperature*, i.e., when grinding a PCB/sand mixture with magnesium metal in the presence of methanol/triglyme. The extent of the dechlorination depends on several parameters. Specific operational parameters of the mill such as rotational speed, kind, size and number of balls were held constant during these studies, so that the milling time and the amount of the dehalogenating agent become the critical parameters (Table I).

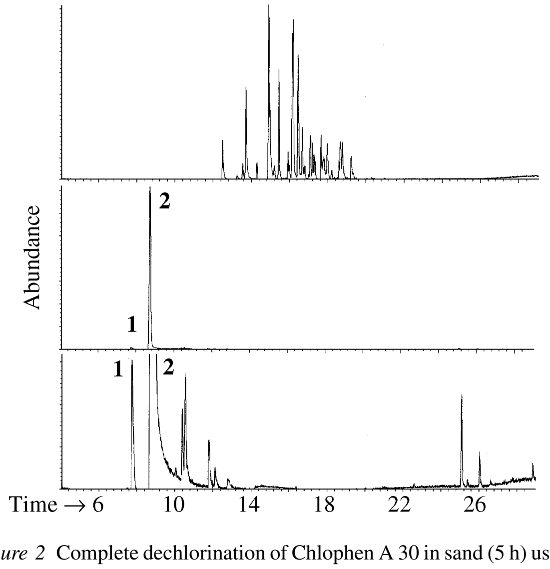

Figure 2 Complete dechlorination of Chlophen A 30 in sand (5 h) using 23 equivalents of magnesium (relative to organically bound chlorine) and methanol/triglyme: top = prior to treatment in a "Retsch S 1" centrifugal ball mill, middle and bottom = after treatment (normal resolution, related to the GC on the top, and high resolution, resp.). Data see Table I (column #1). 1 = phenylcyclohexane, 2 = biphenyl, small peaks represent further, completely dechlorinated species (GC-MS analysis).

Investigations regarding reaction kinetics suggest that the involved mechanisms seem to be identical in principle to those identified in solution. In solution, alkali metals like sodium reductively dehalogenate halogenated aromatic compounds in the presence of hydrogen sources like alcohols or ethers via radical or organometallic intermediates (Fig. 3) [13, 14]. Studies are currently under way to elucidate single steps in detail.

Time-resolved concentration measurements of MC dechlorination of 1,3-DCB (Figs 4 and 5) showed—regardless whether the metal was pre-milled (i.e., pre-activated) or not—that a specific lag phase occurred, followed by a rapid decay of the compound within 10–30 min.

The appearance of the lag phase (Figs 4 and 5) is qualitatively consistent with identical findings during other heterogeneous reactions performed in ball mills involving metals [11]. Elevating slightly the temperature from room temperature to about 70°C only revealed a significant influence on the course of the dechlorination: the lag phase was significantly reduced whilst the curve in the actual decay time window became steeper and steeper, i.e., the total time for the actual decay phase was reduced from appr. 20 min (at 25°C) to appr. 10 min (at 68°C) (Fig. 5). However, pre-milling of magnesium seemed to have no major impact on the total time required for the dechlorination (see Fig. 5 in comparison to Fig. 6 representing runs without pre-milling/activating the magnesium at 25°C). Temporary kinetic analyses of the data gained so far indicate that a specific Langmuir-Hinshelwood-like mechanism might govern the DMCR process in the actual decay phase. A process model will be set up in order to accurately design and adapt DMCR plants regarding different areas of application.

3.2. Accelerating the MC dechlorination

Lowering the reaction time required for a total dechlorination of PCBs towards the magnitude of minutes can be achieved by selecting other hydrogen donors such as simple amines or amides (mainly derivatives of urea) instead of or in combination with alcohols and/or ethers. Such compounds most probably facilitate the production of solvated electrons during milling, which are well known both as very powerful reducing and dehalogenation agents. This strategy can be successfully applied to both contaminated materials and virtually pure pollutants: *pure* PCBs (Chlophen A 30) could be entirely converted to biphenyl within *15 min* by using magnesium and amine (ratio PCB:Mg:amine = 1:1–2:3–5 (w/w/v)). Hence, DMCR makes it possible to get magnesium chloride and biphenyl in high yields which can be used/sold as valuable chemical compounds. Biphenyl isolation demonstrated a 90–94% recovery of biphenyl (mole/mole) [10].

Amine-mediated MC reductive dechlorinations of DCB already shown above in Figs 4 and 5 represent reaction conditions which were carried out with

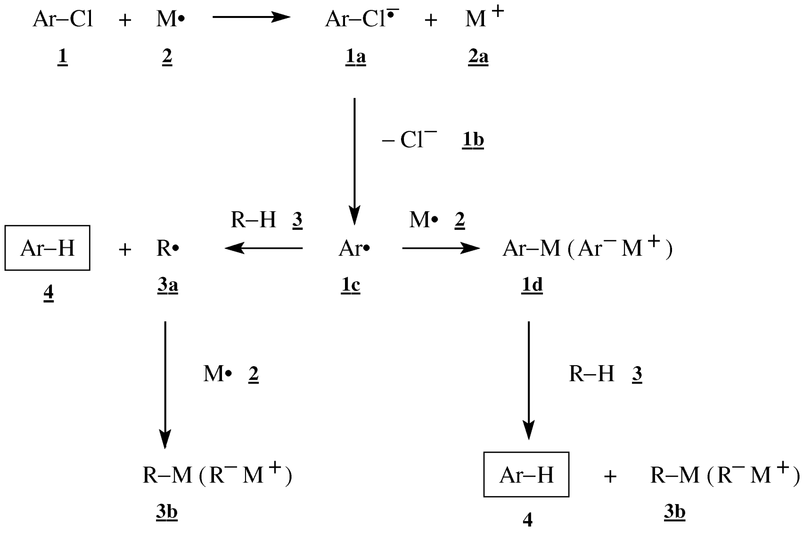

Figure 3 Reductive dechlorination of chlorinated aromatics (arylchlorides, Ar-Cl) by alkali metals in solution in the presence of hydrogen donors (R-H) like ethers or alcohols, compiled according to former publications [13, 14].

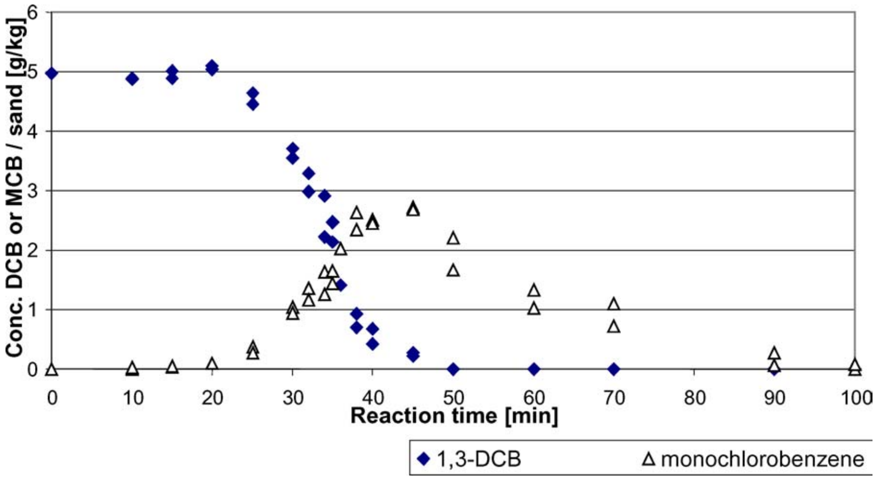

Figure 4 Complete reductive dechlorination of 1,3-DCB over time in a sand slurry with magnesium, *n*-butylamine and cyclohexane (inert diluting agent) using a centrifugal ball mill (Retsch S 1000) at 25°C. Benzene (not shown here) is the single and final dechlorination product.

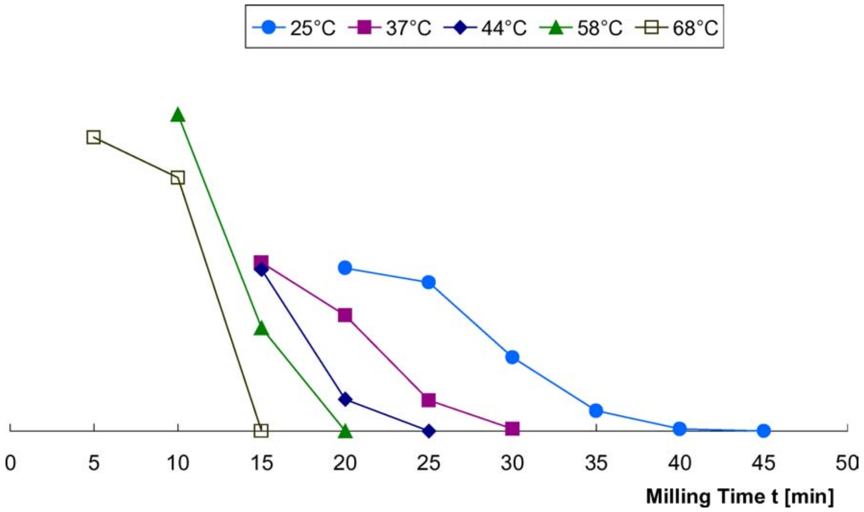

Figure 5 Temperature-dependent reductive dechlorination of 1,3-DCB over time in a sand slurry with pre-milled (pre-activated) magnesium, *n*-butylamine and cyclohexane using a Retsch S 1000 centrifugal ball mill (not to scale regarding the axis of ordinates; furthermore, DCB was employed in two different initial concentrations; data represent the average values of duplicate or triplicate runs).

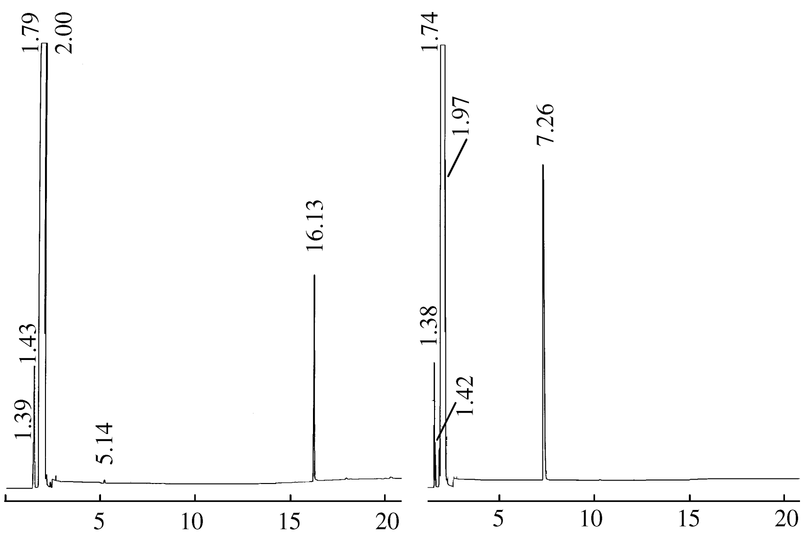

Figure 6 Complete reductive dechlorination of PCP to phenol in sand during milling for *30 min at room temperature* with magnesium and ethylenediamine: left = prior to treatment in a Retsch S 1000 centrifugal ball mill, right = after treatment (according to GC-FID analysis).

diluted reagents to increase reaction times and to expand/distend the time range for improved kinetic measurements/data observations. Under normal conditions, DCB can be completely dechlorinated to benzene within a few *minutes* only, if required.

PCB contaminated transformer oils can be especially rapidly decontaminated *and recycled* under such conditions, because the pollutants are destroyed under benign conditions *at room temperature* [10].

PCB dechlorination does not occur stoichiometrically. For example, a certain excess of magnesium is required to achieve complete dechlorinations (i.e., at least 16 equivalents related to organic bound chlorine, according to Table I). With sodium, at least seven equivalents in similar experiments are required. That observation can be explained by unavoidable side reaction in which biphenyl is further reduced by sodium via phenylcyclohexenes to phenylcyclohexane. This compound is also generated with magnesium (see Fig. 2), however in significantly lower amounts that can hardly account for the significant excess magnesium necessary. Hence, it seems more likely that the excess of this metal needed to accomplish total dechlorinations, either in solid or liquid materials, may be chiefly attributed to diluting effects of the solid or liquid matrix. Further investigation pertaining to this issue is under way.

Regarding magnesium, experimental data suggest that multiple, coupled Grignard-Zerewitinoff-like reactions may represent one major reaction path here. Interestingly, common laboratory Grignard reactions can be always conducted in solution only. In addition, these procedures usually require very dry solvents, highly purified reagents and a protective gas atmosphere in order to be accomplished successfully. Even traces of proton donors have to be strictly avoided. Apparently, Grignard or Grignard-like reaction without strictly purified reagents, even in the presence of large amounts of a proton donor, can be carried out with ball milling. Moreover, the intermediary Grignard or Grignard-like compound is subsequently protonated at once by the proton donor.

In general, the reactivity of the base metal governs the reaction time. Regarding DMCR treatment of PCB, the dechlorination power of the deployed metal declines in the following series, qualitatively coinciding with a decreasing reduction potential: Na $>$ Mg $>$ Al $\gg$ Zn, Fe. Therefore, the type of the metal *and* the hydrogen source were identified as decisive chemical parameters in the DMCR approach as well. Approaches for further speeding up dechlorinations of PCBs in natural soils, filter dusts and transformer oils are permanently tested and scaled up using highly efficient, eccentric vibratory mills such as an "ESM 234" device (SIEBTECHNIK GmbH, Mülheim/Ruhr, Germany) [12].

3.3. Dechlorination of PCP in solid matter

It was verified that other toxic and recalcitrant polychlorinated aromatics can be rapidly and entirely dechlorinated in the same manner as PCBs or 1,3-DCB. According to Fig. 6, PCP was completely converted to phenol as the sole product, simply by using appr. 5% magnesium and 3% amine regarding the solid matrix (sand) (w/w). The dechlorination proceeded via partly dechlorinated chlorophenols only: as for PCBs or DCB, partly dechlorinated intermediates could be identified by GC analyses using analytical standards of these compounds during time-resolved measurements.

4. Discussion and conclusions

Mechanochemistry has been examined during the last 10 years for dehalogenation of PCBs, PCP, pesticides, and PCDD/Fs in soil, sediments, liquids, and building debris.

MC dehalogenation is accomplished by mixing waste material with chemical reagents in a vibratory, planetary, centrifugal or similar ball mills, of which vibratory mills are available for throughputs of materials up to several tons per hour. Reactions occur because of the finely divided nature of the reagents and the energy imparted by colliding balls. The observed products and proposed reaction pathways are consistent with radical and organometal intermediates and provide confidence in understanding these reactions. Reaction rates are proportional to the impact energy, which depends on the number of colliding balls, rotational speed, and the ratio of chemical reagents to waste constituents.

During the 1990's, Australian workers patented a ball mill process using calcium oxide or metals as the primary reagents for destroying highly concentrated DDT and PCB-containing wastes [2–4]. Reaction rates are slow, on the order of 6–12 h, and reaction products from this process [4] are complex and present a potential regulatory and public concern.

The DMCR method uses small amounts of metals and hydrogen sources, such as magnesium and alcohols, polyethers or amines, to treat the waste. PCBs in solid or liquid matrices can be destroyed to non-detectable concentrations (GC MS, GC ECD) in a period of minutes to hours. The reaction pathway for this process is well-defined as demonstrated by the isolation and recovery of over 90% of biphenyl, the dechlorinated product of PCBs. The other major reaction product is magnesium chloride. DMCR, which has been carried out in laboratory and pilot studies, yields acceptable, defined reaction product at much faster rates than the calcium oxide process. These advantages lead to greater throughput, improved economics, and regulatory and public acceptability. Critical cost parameters are pollutant concentration, metal and promoter concentration, and water content of the waste. For the case of a small ball mill capable of holding 0.85 tons (2,000–10,000 tons/year) of waste, operating costs (utilities, labor, maintenance, parts, chemicals, and analytical) and capital costs (3-year depreciation) are calculated at $ 140–450/ton for waste containing 1,000–10,000 ppm PCB and water contents of 15%.

DMCR offers the following benefits:

1. A cost-effective treatment alternative for PCB, dioxins, and pesticides for small or remote sites, for which conventional disposal is unattractive. Even highly concentrated pollutants, e.g., pure PCB oils or pesticides such as hexachlorocyclohexane, can be readily converted to valuable, less toxic chemical compounds in high yields under benign conditions, i.e., biphenyl and trichlorobenzene or cyclohexane, resp., which can be rationally utilized in process streams or marketed.
2. An effective method for treating PCB and dioxin residuals from on-site, indirect thermal desorption processing, liquid residues, or building debris.
3. A treatment method for dioxins in solids, for which no current treatment facility exists.
4. Reduced potential emissions to the environment increase regulatory and public acceptability because the process operates at ambient conditions in a closed system and generates no gaseous emissions.

References

1. M. ARESTA, A. DIBENEDETTO and T. PASTORE, in Proceedings of the CONSOIL 2003 Conference (8th International FZK/TNO Conference on Contaminated Soil), Gent, Belgium, 12–16 May 2003 (Computer Optical Disk ISSN: 0947-8620).
2. S. A. ROWLANDS, A. K. HALL, P. G. MCCORMICK, R. STREET, R. J. HART, G. F. EBELL and P. DONECKER, *Nature* **367** (1994) 223.
3. P. DONECKER, P. G. MCCORMICK, R. STREET and S. A. ROWLANDS, PCT WO94/14503 (1994).
4. A. K. HALL, J. M. HARROWFIELD, R. J. HART and P. G. MCCORMICK, *Environ. Sci. Technol.* **30** (1996) 3401.
5. S. LOISELLE, M. BRANCA, G. MULAS and G. COCCO, *ibid.* **31** (1997) 261.
6. E. GOCK, M. OPEL and J. MAYER, *Organohalogen Comp.* **54** (2001) 185.
7. T. IKOMA, Q. ZHANG, F. SAITO, K. AKIYAMA, S. TERO-KUBOTA and T. KATO, *Bull. Chem. Soc. Jpn.* **74** (2001) 2303.
8. V. BIRKE, *TerraTech* **5** (1998) 52.
9. *Idem.*, in Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, edited by A. R. Gavaskar and A. S. C. Chen (Monterey, USA, May 2002) (Battelle Press, Columbus, USA, Computer Optical Disk, ISBN 1-57477-132-9).
10. V. BIRKE, J. MATTIK, D. RUNNE, H. BENNING and D. ZLATOVIC, in Proceedings of the CONSOIL 2003 Conference (8th International FZK/TNO Conference on Contaminated Soil), Gent, Belgium, 12–16 May 2003 (Computer Optical Disk ISSN: 0947-8620).
11. G. HEINICKE, "Tribochemistry" (Akademie-Verlag, Berlin, 1984).
12. TRIBOCHEM, Web site http://www.tribochem.de.
13. J. HAWARI, *J. Organomet. Chem.* **437** (1996) 91.
14. J. G. SMITH and I. HO, *J. Org. Chem.* **38** (1973) 3601.

Received 11 September 2003
and accepted 27 February 2004