



## Mechanochemical destruction of mirex co-ground with iron and quartz in a planetary ball mill

Yunfei Yu, Jun Huang, Wang Zhang, Kunlun Zhang, Shubo Deng, Gang Yu \*

State Key Joint Laboratory of Environment Simulation and Pollution Control (SKJLESPEC), School of Environment, POPs Research Center, Tsinghua University, Beijing 100084, PR China

### HIGHLIGHTS

- ▶ Mirex was quickly completely destroyed when co-ground with iron powder and quartz sand.
- ▶ Model was established to well correlate the efficiency with main operational parameters.
- ▶ Main products were identified as carbon and ferric chloride, with no organic residue found.
- ▶ Mechanism was proposed as dechlorination followed by carbonization.

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### ABSTRACT

Mechanochemical destruction (MCD) has been recognized as a promising non-combustion technology for the disposal of obsolete pesticides belonging to the persistent organic pollutants (POPs). Mirex, a termiticide ever used for many years in China, was ball milled in the presence of various reagent(s) in a planetary ball mill at room temperature to investigate the destruction efficiency. The ground samples were characterized and analyzed by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, gas chromatography (GC), and ion chromatography (Martins, Bicego et al.). Under the same conditions of mill rotary rate and charge ratio, the mixture of iron powder and quartz sand (Fe/SiO<sub>2</sub>) was found best in promoting the mirex destruction. Mirex was completely destroyed after 2 h grinding at a charge ratio of 36:1 (reagent/mirex, m/m) and a mill rotation speed of 550 rpm. No organic compound was detected by GC/μECD screening. The yield of water-soluble chlorine determined by ion chromatography (Martins, Bicego et al.) in the final residue accounted for 90.7% of chlorine in the original mirex, which indicated a nearly complete dechlorination. Signals of both graphite and amorphous carbon were found in the Raman spectra of the co-ground powder samples. With the main final degradation products of water soluble Cl and carbon, the mechanism of the mechanochemical destruction approach should be dechlorination followed by the carbonization.

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### 1. Introduction

Mirex (C<sub>10</sub>Cl<sub>12</sub>, CAS No.: 2385-85-5) is a fully chlorinated synthetic compounds with a cage-like structure, which was used in large quantities as a pesticide to control fire ants or termites, as well as a flame retardant in plastic materials. In 1970s, the concerns were raised about its extreme persistence, toxicity and bioaccumulation in food chains, which finally led to USEPA's decision to eventually ban the use of mirex against the imported fire ant in 1976 (Kaiser, 1978). In 2001, mirex was listed in the Stockholm Convention on the persistent organic pollutants (POPs), which requires a global ban of the production and use and the environmentally sound management (ESM) and disposal of obsolete stockpiles.

China started research on mirex in 1969 and the Shanghai Electrochemical Plant tentatively produced mirex from 1970 until the production facility was dismantled in 1975. The produced mirex was either exported to Tanzania and Zambia for a government railroad project or sold to some other provinces within China. Thereafter, several manufacturers started to produce mirex around 1986, and there were three manufacturers with production facilities remained with 30 t year<sup>-1</sup> production by the end of 2004 (Wei et al., 2007; Hu et al., 2007). For implementing of the Stockholm Convention, China banned the production and use of mirex as well as other pesticides of the "dirty dozen" in 2009 (Li, 2009). However, obsolete stockpiles in termite control stations and contaminated sites around former productions are still awaiting ESM and disposal and remediation activities.

Considering the potential formation and release of dioxins from the incineration disposal of chlorinated POPs waste, non-combustion

\* Corresponding author. Tel.: +86 10 6278 7137; fax: +86 10 6279 4006.  
 E-mail address: [yg-den@tsinghua.edu.cn](mailto:yg-den@tsinghua.edu.cn) (G. Yu).

technologies have received more attentions in recent years. Among various options, mechanochemical destruction (MCD) based on high energy ball mill has been identified as a promising technology for the disposal of POPs wastes due to its advantages over other conventional chemical methods in solid waste disposal (Guo et al., 2010). For example, “Mechanochemical Dehalogenation” has been recognized by USEPA as one of “Full scale technologies for treatment of POPs”, which has been used to treat DDT, aldrin, dieldrin and lindane (USEPA, 2010). The typical MCD process is to grind POPs wastes with specific reagents in high energy planetary or vibratory ball mills, utilizing mechanical energy to activate chemical reactions and induce structural changes of target chemicals. Depending on the reagents used, there are several types of main MCD technologies developed, including:

- (1) The most classic approach is to use calcium oxide (CaO), which has been widely applied for destroying various POPs such as 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane (DDT), octachlorinated dibenzo-*p*-dioxin and furan (OCDD/OCDF), pentachlorophenol (PCP), dechlorane plus (DP), and pentachloronitrobenzene (PCNB). The final products are mainly inorganic carbon and chloride (Rowlands et al., 1994; Hall et al., 1996; Tanaka et al., 2003; Nomura et al., 2005; Wei et al., 2009; Zhang et al., 2010, 2011). Quartz, a low cost and largely available material, has been found to prompt the degradation efficiency of chlorinated POPs like PCBs (Zhang et al., 2001).
- (2) DMCR (i.e. “Dehalogenation by Mechanochemical Reaction”) method which grinds the waste with alkali or alkaline-earth metals (e.g. magnesium, aluminum, sodium, zinc, aluminum, iron) in combination with certain hydrogen donors (e.g. alcohols, ethers, amines). It has been used for the dechlorination of polychlorinated biphenyls, pentachlorophenol, and 1,3-dichlorobenzene (Birke et al., 2004, 2006, 2011; Nah et al., 2008). Here the detected final products are mainly their parent hydrocarbons, which mean the reaction mechanism is the dechlorination instead of complete destruction.
- (3) Manganese oxides based methods, e.g. the mechanochemical degradation of atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) adsorbed on synthetic pyrolusite ( $\beta$ -MnO<sub>2</sub>), birnessite ( $\gamma$ -MnO<sub>2</sub>), and cryptomelane types I and II ( $\alpha$ -MnO<sub>2</sub>) (Shin et al., 2000); and to grind 2,4-dichlorophenoxyacetic acid (2,4-D) with synthetic birnessite ( $\gamma$ -MnO<sub>2</sub>) (Nasser et al., 2000).
- (4) Hydrides based mechanochemical methods, e.g. to grind polychlorinated biphenyls (PCBs) with NaBH<sub>4</sub> (Aresta et al., 2003), to grind chlorobenzene and hexachlorobenzene with CaH<sub>2</sub> (Loiselle et al., 1997; Mulas et al., 1997; Cao et al., 1999). However, grinding operations have to be carefully conducted because of the potential occurrence of an explosive type reaction when CaH<sub>2</sub> is used (Zhang et al., 2001).

Also in our previous work, fine iron powder has been successfully used to destroy PCNB when co-grinding in a planetary ball mill. Unlike DMCR, here the solvents as hydrogen donors are not necessary (Zhang et al., 2011). Therefore, considering the low cost, good reactivity, easy availability and non-toxicity, the most promising reagents used in engineering application might include CaO, fine iron powder as well as additional quartz. In the present study, various compositions of these reagents were investigated for the destruction efficiency of mirex by high energy ball milling. The most efficient process was then optimized for its operational parameters including charge ratio and rotation speed. Based on the experiment data, a model was established to correlate the kinetic constant with operational parameters, which should be use-

ful to predict the destruction kinetic constants under different experimental conditions and for upscaling to full scale operation. In addition, the degradation mechanism was proposed based on the results from both chemical analysis and surface characterization.

## 2. Materials and methods

### 2.1. Samples and chemicals

Mirex (C<sub>10</sub>C<sub>12</sub>, 90% in purity) was provided by Suzhou Jiangfeng Termiticide Co., Ltd. (Jiangsu, China). Fine iron powder (Fe, 98% in purity) and calcium oxide (CaO, 98% in purity) were purchased from Beijing Modern Eastern Fine Chemicals Corporation (Beijing, China). Quartz sand (SiO<sub>2</sub>, 98% in purity) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). CaO was heated at 800 °C for 4 h and stored in a dryer prior to use. Hexane of HPLC grade used for sample extraction and clean-up were purchased from Baker Inc. (New Jersey, USA).

### 2.2. MCD experiments

A QM-3SP2 planetary ball mill manufactured by Nanjing University Instrument Corporation (Nanjing, China) was used for the ball milling experiments. Mirex powder was firstly mixed with various reagents at a mass ratio of 1:24, including CaO, CaO + SiO<sub>2</sub>, Fe, Fe + SiO<sub>2</sub>, and SiO<sub>2</sub>, thus yield to feed-in mixtures. One portion (5.0 g) of each feed-in mixture, containing 0.2g mirex and 4.8g reagent(s), was then introduced into the stainless steel pot containing 180g of stainless steel balls ( $\Phi$ 5.60 mm). The planetary ball mill was operated at the speed of 550 rpm; with the rotation direction of supporting disk automatically shifted every 30 min. The feed-in mixture corresponding to the highest destruction efficiency of mirex was selected for the optimization of the charge ratio as well as the rotation speed of the mill. For such purpose, a series of ball milling experiments with four amount levels of selected feed-in mixture (5g, 6g, 7.2g, and 9g) under four rotation speed levels (550 rpm, 500 rpm, 450 rpm, 400 rpm) were conducted. Defining the charge ratio ( $C_R$ ) as the mass of the balls divided by that of the feed-in mixture was defined as the, the four rotation speed levels above are corresponding to the  $C_R$  of 36:1, 30:1, 25:1 and 20:1. When additional quartz is involved, the proportion of quartz sands is 10% of total mass of charged reagent.

### 2.3. Analysis method

An aliquot (0.05 g per batch) of each milled mixture was ultrasonically extracted with hexane, and centrifugalized at 3000 rpm for 15 min to remove the solids from the extraction. Mirex and possible chlorinated degradation products were analyzed using an Agilent 6890 plus gas chromatography equipped with a microelectron capture detector (GC/ $\mu$ ECD; Agilent, USA) and a DB-5MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m). Nitrogen (99.999% in purity) was used as carrier gas at a constant flow of 34.5 mL min<sup>-1</sup>. GC oven temperature was programmed initially from 60 °C (held for 1 min) to 240 °C at 25 °C min<sup>-1</sup>, and increased to a final temperature of 300 °C (held for 5 min) at 5 °C min<sup>-1</sup>. Both GC inlet and  $\mu$ ECD detector were conditioned at 280 °C. One microliter of the extraction was auto-injected at the splitless mode.

Another portion (0.05 g per batch) was used for the determination of chloride content from the dechlorination of mirex. The sample was ultrasonically agitated in 20 mL deionized water at 80 °C for 20 min, and centrifugalized at 3000 rpm for 15 min. The separated solid residue was extracted one more time in the same manner. The final solution was analyzed for chloride ions by a

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