



# Effects of zero-valent metals together with quartz sand on the mechanochemical destruction of dechlorane plus coground in a planetary ball mill



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## HIGHLIGHTS

- Mechanical destruction of dechlorane plus was prompted by Aluminum powder.
- Main products include carbon and chloride, and no organic component remaining.
- Formation of Si–Cl bond explains why detected  $\text{Cl}^-$  was less than Cl in original DP.
- Dechlorination followed by carbonization is proposed as the main mechanism.

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## ABSTRACT

Mechanochemical destruction by grinding with additives in high energy ball milling has been identified as a good alternative to traditional incineration for the disposal of wastes containing halogenated organic pollutants. Despite CaO normally used as an additive, recently Fe + SiO<sub>2</sub> has been used to replace CaO for a faster destruction. In the present study, zero-valent metals (Al, Zn, besides Fe) together with SiO<sub>2</sub> were investigated for their efficiencies of prompting the destruction of dechlorane plus (DP). Aluminum was found of be the best with a destruction percentage of nearly 99% for either *syn*- or *anti*-DP after 2.5 h milling. In comparison, only 88/85% and 37/32% of *syn*-/*anti*-DP were destroyed when using zinc and iron after the same time, respectively. The detected water soluble chloride was lower than the stoichiometric amount containing in the original DP samples, due to the Si–Cl bond formed during the process. The potential fate of C and Cl present in DP is in the form of inorganic carbon, inorganic Cl and formation of Si–Cl bonds, respectively. The results suggested that Al + SiO<sub>2</sub> is promising in the mechanochemical destruction of chlorinated organic pollutants like DP.

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## 1. Introduction

Environmentally sound destruction of solid wastes containing organohalogen materials is a challenging issue. When using incineration technology, toxic by-products such as polyhalogenated dibenzo-*p*-dioxins and dibenzofurans might be formed due to the high content of halogen. Therefore developing non-combustion alternative technologies to incineration for the destruction of organohalogen materials has received great interests from both the academy and the industry. Among various existing technologies developed, mechanochemical destruction (MCD) based on grinding waste with proper additives in high energy ball milling has been identified as a promising option; for example USEPA has listed

“Mechanochemical Dehalogenation” as one of “Full scale technologies for treatment of persistent organic pollutants (POPs)” [1].

In 1994, Rowlands et al. first reported the MCD of DDT using calcium oxide (CaO), by which DDT was completely destroyed and transformed into CaCl<sub>2</sub> and graphite after 12 h ball milling [2]. Since then, calcium oxides as additive have been widely applied for mechanochemical destruction of various POPs. For example, CaO is applied for destruction of octachlorinated dibenzo-dioxin and furan [3], pentachlorophenol [4], dechlorane plus (DP) [5], and trichlorobenzene [6]. The final products from mechanochemical reaction using CaO are mainly inorganic carbon and chloride. However, the destruction efficiency using CaO becomes quite low for highly concentrated POPs wastes, which might be caused by the facts that CaO can easily absorb moisture and carbon dioxide in the air. In addition, Mn-oxides as additives are successful of destruction such as phenanthrene [7], pentachlorophenol [8], among others with the final produces achieving carbonization.

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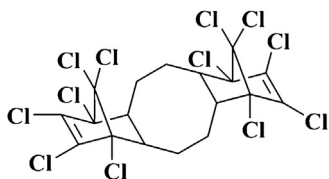


Fig. 1. Structure of dechlorane plus (DP).

Despite that oxides were normally used as additives, recently the combination of iron powder (Fe) and quartz sand ( $\text{SiO}_2$ ) has been tried to replace oxides for a faster destruction. For both cases of organochlorine mirex [9] and organobromine tetrabromobisphenol A (TBBPA) [10], the destruction efficiencies using Fe +  $\text{SiO}_2$  are significantly higher than those using oxides under comparable operational conditions. During the ball milling process, the zero-valent iron powder is supposed to provide electrons to dehalogenate the target chemical, while the cleavage of quartz sand will generate silicon containing radicals which can quickly react with the original chemical as well as the dehalogenated intermediates [9,10]. Therefore it is possible to introduce zero-valent metals that exhibit more reductive capability than iron to further improve the destruction efficiency.

DP (CAS No. 13560-89-9) is a chlorinated flame retardant with high production volume, which has been widely used in polymers for coating electrical wires and cables, connectors used in computers and plastic roofing material in polymeric systems since 1960s [9]. Since 2006, concerns have been aroused about their persistence, bioaccumulation and toxicity (PBT) of DP [11–13]. Scientific evidences have revealed that DP may possess characteristics of POPs [14–20], which may recruit in a global ban in the future conference concerning the Stockholm Convention.

Further to our previous study on the MCD of DP using CaO as well as the successful practice of prompting the MCD efficiency of mirex and TBBPA using the mixture of iron powder and quartz sand (Fe +  $\text{SiO}_2$ ) [5,9,10], the present study is aiming at improving the MCD efficiency of DP using the mixture of more reductive zero-valent metal and quartz sand. For such purpose, Al, Zn and Fe were investigated for their effects on the MCD efficiency of technical DP when co-grinding together with quartz sand in a planetary ball mill. The most efficient process was then optimized for its operational parameters, including the charge ratio of material and the grinding media. In addition, the potential fate of C and Cl present in DP was proposed base on the results from both chemical analysis and surface characterization.

## 2. Materials and methods

### 2.1. Chemicals and materials

DP ( $\text{C}_{18}\text{H}_{12}\text{Cl}_{12}$ , 99% in purity, Fig. 1), a technical DP product, was purchased from Jiangsu Anpon Electrochemical (China). The percentage of *anti*-DP and *syn*-DP in the primary material is about 75% and 25%, respectively. Aluminum powder, zinc powder, iron powder (Al, Zn, Fe,  $\geq 98\%$  in purity, all 300 mesh in size), and quartz sand ( $\text{SiO}_2$ ,  $\geq 99.8\%$  in purity) were obtained from Sinopharm Chemical Reagent (China). All solvents (methanol, hexane and acetone) used for extraction and clean-up were of HPLC grade or higher (J.T. Baker, USA). All chemicals were used as received without further purification.

### 2.2. Ball milling experiments

A planetary ball mill (QM-3SP2, Nanjing University Instrument, China) was used in all experiments. A stainless 80 mL vial was filled

with stainless balls in diameter of between 5 mm and 10 mm, which serve as the milling medium. Zero-valent metal (Al, Zn, Fe) and quartz sand were individually added as reactive chemicals during ball milling of DP. The detailed experimental parameters, such as weight ratio, metal/ $\text{SiO}_2$  molar ratio and (metal +  $\text{SiO}_2$ )/DP mass ratio were listed in Table 1. The mixture was placed in the covered stainless vial containing balls in ambient air and placed onto the planetary ball mill, which was operated at a rotary speed of the main disk of 275 rpm and the rotation direction changed automatically every 30 min.

### 2.3. Sample analysis

0.01 g of each milled mixture was ultrasonically extracted with hexane, and centrifugalized at 3000 rpm for 15 min to remove any solids from the extraction. DP and possible chlorinated degradation products were analyzed using an Aglient 6890 plus gas chromatography equipped with a microelectron capture detector (GC/ $\mu\text{ECD}$ ; Agilent, USA) and a DB-5MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). Nitrogen (99.999% in purity) was used as carrier gas at a constant flow of 34.5 mL/min. GC oven temperature was programmed from 140  $^\circ\text{C}$  (held for 1 min) to 250  $^\circ\text{C}$  at 30  $^\circ\text{C}/\text{min}$ , and to a final temperature of 285  $^\circ\text{C}$  at 0.8  $^\circ\text{C}/\text{min}$  (held for 5 min).

Another 0.05 g sample was taken for the determination of water soluble chloride in the milled mixture. The sample was ultrasonically agitated in 50 mL deionized water at 60  $^\circ\text{C}$  for 30 min, and centrifugalized at 3000 rpm for 15 min. The separated solid residue was extracted twice for inorganic contents. The combined solution was concentrated using gentle nitrogen flow and analyzed for chloride ions by a DX-1000 ion chromatography (IC) (Dionex, USA) equipped with an Ion-Pac AS4A-SC anion exchange column.

### 2.4. Identification of final products

Crystalline products were identified by X-ray Powder Diffraction (XRD, Rigaku D/max-rB, Japan) using the following settings: Cu  $K\alpha$  radiation, 40 keV accelerating voltage, 80 mA current, 10–90  $^\circ$   $2\theta$  scanning range, 0.02  $^\circ$  step and 6  $^\circ/\text{min}$  scan speed. Raman spectra were recorded at room temperature using a Microscopic Confocal Raman Spectrometer (Renishaw RM 2000, UK) with Ar-laser beam at the 514.5 nm line. The composition of ultimate products was detected by X-ray Photoelectron Spectrometry (XPS) (Thermo Scientific ESCALAB 250Xi) with Al  $K\alpha$  X-ray source. The binding energy scale was calibrated by  $\text{C}_{1s}$  peak of 284.8 eV in XPS measurement.

## 3. Results and discussion

### 3.1. Performance comparison for using different metals

DP was co-ground with the mixture of different zero-valent metal powder and quartz sand (i.e. Al +  $\text{SiO}_2$ , Zn +  $\text{SiO}_2$  and Fe +  $\text{SiO}_2$ ), respectively. The detailed conditions are as shown in Table 1. The amount of residual DP after 1 h ball milling was measured and summarized in Fig. 2. The destruction efficiency of DP

Table 1  
Detailed experimental parameters of reductive composites with different metals.

Sample no.	Metal	Metal/ $\text{SiO}_2$ molar ratio	(Metal + $\text{SiO}_2$ )/DP mass ratio	$C_R$
S1	Al	1:1	11:1	20
S2	Zn	1:1	11:1	20
S3	Fe	1:1	11:1	20
S4	Al	22:1	11:1	30

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