Mechanochemical degradation of chlorinated contaminants in fly ash with a calcium-based degradation reagent

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A B S T R A C T

This report presents our results in a low-temperature mechanochemical hydrodechlorination process applied to fly ash coming from a municipal waste incinerator in order to efficiently remove all traces of PCDDs, PCDFs and PCBs. We found that the most suitable degradation agent is a mixture of metallic calcium and calcium oxide. A sample of fly ash presenting a TEQ of 5200 pg g^{-1} was completely detoxified (no traces of PCDDs, PCDFs and PCBs detected) after ball-milling at 400 rpm over night.

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1. Introduction

The hydrodechlorination processes are a widely investigated class of chemical reactions with direct application in depollution treatments of various contaminated substrates with harmful chemicals such as polychoro-dibenzodioxins (PCDDs), polychloro-dibenzofurans (PCDFs) or polychlorobiphenyls (PCBs). The past few years saw, along with the development of the classic types of activation (thermal, photochemical or chemical), the emergence of a new panel of useful applications of one of mankind's oldest technology, grinding, in what came to be known as mechanochemical processes. In the hydrodechlorination field, these new activation-type methods started to make their own little niche, becoming the mechanochemical dechlorination processes (MDP). These are a series of procedures that are using, along with the contaminated substrate, a hydrodechlorination additive, both being introduced in a ball mill. Among calcium species used in such MDP, the preferred reagent is by far CaO (Hall et al., 1996; Ikoma et al., 2001; Zhang et al., 2001; Mio et al., 2002; Tanaka et al., 2003; Inoue et al., 2004; Aresta et al., 2005; Nomura et al., 2005;

Yan et al., 2007; Wei et al., 2009), but Ca(OH)$_2$ (Zhang et al., 2001; Birke et al., 2004), CaCO$_3$ (Tongamp et al., 2008) or CaH$_2$ (Loiselle et al., 1997; Monagheddu et al., 1999) were also used. However, the reported results depend highly on the chosen substrates for dechlorination. Thus, DDT was almost completely degraded after a 24 h treatment, in a water-free environment, under N$_2$ atmosphere (Hall et al., 1996), while in the same conditions degradation yields for PVC range from 20% to 80% (Inoue et al., 2004) (moreover, a molar ratio 1:4 between PVC chlorine and CaO is needed). For their part, 3- or 4-chloro-biphenyls are also hydrodechlorinated in a 99% proportion (Zhang et al., 2001; Nomura et al., 2005), although a supplement of quartz is added in the milling process (increasing thus the amount of final waste).

When it comes to the MDP applied to PCDDs, PCDFs or PCBs, the reported results in the use of CaO present mixed rates of success. For instance, Yan and coworkers reported a 60% dechlorination yield for PCDDs/PCDFs in fly ash from a medical incinerator, after 2 h (Yan et al., 2007), while Nomura et al. in a mechanistic study, found that the two octa-chlorinated congeners, OCDD and OCDF, are almost completely dechlorinated after 8 h (Nomura et al., 2005). A complete degradation of PCBs from transformer oil was obtained by Birke (Birke et al., 2004), although in this case, along CaO and Ca(OH)$_2$, a more potent Mg/MeOH reductive system was used in the MDP. In his study, Monagheddu reported an almost complete dechlorination of soil samples artificially polluted with

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PCDDs and PCDFs, using CaH$_2$ under an Ar atmosphere (Monagheddu et al., 1999). Pentachlorophenol was completely dechlorinated by CaO, but only upon addition of quartz sand (Wei et al., 2009).

Among the disadvantages of these processes, the necessity of dry, water-free, conditions as well as operating at higher temperatures or pressures are major set-backs when considering the costs of an industrial application. Nevertheless, the use of CaO in hydrodechlorination MDP processes found some practical applications (*e.g.* the New-Zealander *Environmental decontamination* or the Japanese *Radicalplanet* processes), but from the limited data available on the internet (Noma, 2002; Vijgen, 2002), it appears that the quantities of CaO are rather high, which is a major setback of these methods considering the input of Ca ions in waste waters, with a subsequent increase of their durity.

Calcium as a metal have been never used in such a purpose, in a mechanochemical process. Although our own procedure for the hydrodechlorination of PCDDs, PCDFs and PCBs using a mixed, heterogeneous system of metallic calcium, Rh/C and an alcohol is an effective one (Mitoma et al., 2001, 2004, 2006, 2009a,b), in our continuous search for improvement we decided to explore the niche of metallic calcium utilization in a MDP and compare the results with other MDP procedures simultaneously carried out. There is a certain advantage when working with metallic calcium, compared to the use of other metals: for instance, the use of sodium is limited due to its high reactivity; in comparison, metallic calcium is readily coated with a film of calcium carbonate, making this secondary group metal easy to handle, but this does not represent any restriction for its use, since this coating will be swiftly crushed during the MDP.

2. Experimental

2.1. Fly ash characteristic samples preparation

Fly ash (FA) samples were randomly collected, in several different days, from a Hiroshima prefecture municipal waste incinerator (MWI) having a capacity of 30 t d^{-1} burned domestic waste. Those samples presented a total content of PCDDs, PCDFs and PCBs ranging from 2100 to 7600 TEQ pg g^{-1} fly ash. The samples were dried at 107 °C (Program System Furnace F-120-SP electric oven, Tokyo Glass TGK Company), sieved and only particles with a diameter less than 2 mm (about 95% of the initial quantity) were further used. A thorough mixing in a pot-mill rotation table (100 rpm, NITTO Science Company) to a basic contaminated fly ash completed the final representative composite sample, with an overall 4000 TEQ pg g^{-1}. From this composite sample, a quantity of 90 g was drawn and washed with demineralized water through ultrasonication in an Ultrasonic Multi-cleaner W-118 (Honda Electronics Company) during 30 min., using a 28, 45 and 100 kHz frequencies (in cycles of 1 s each), and separated from the aqueous layer through filtration on a Millipore membrane filter (0.45 μm). The solid residue was dried in a furnace at 107 °C (to a maximum moisture content of 1.4%) and subsequently divided in six equal parts of about 10 g each, representing the starting material for each MDP (see Section 3).

2.2. General procedure for the planetary ball-milling of solid samples and analysis of the residue

All reagents were used as purchased, without any prior treatment. All experiments were carried out using a Retsch PM-100 ball mill, working at 400 rpm and a rotation-to-revolution ratio of 1 to −2 (doubling thus the inverse rotation force compared to the direction of the orbital motion). A mixture of fly ash (~10 g) and addi-

tive (ratio 100:1, in weight) was introduced in a 250 mL stainless steel pot along with 20 stainless steel balls (10 mm diameter). The milling time in each case was 20 h. After this period, a 1.0 g quantity of fly ash was then collected and analyzed for PCDDs, PCDFs and PCBs concentrations. These concentrations, expressed as TEQ content, were determined according to Japanese standard regulations in vigor (JIS, 1999a,b). The solid reaction mixture was poured into 1 M nitric acid and extracted twice using dichloromethane under vigorous shaking. After separation from the aqueous layer, the combined organic phases were washed with distilled water until the pH of the aqueous layer became neutral. The dichloromethane layer was dried on anhydrous MgSO$_4$, then filtered and concentrated to 10 mL. For measurement of the PCDDs, PCDFs and PCBs concentration, the GC–ECD analysis conditions were the following. GC analyses were carried out using a gas chromatograph (GC-14B; Shimadzu Corp.) equipped with a 2 m glass column (i.d. 3.0 mm, column packing: OV-17, 2% Chromosorb WAW DMCS 80/100), with N$_2$ as the carrier gas. The injection was performed in a splitless mode. The detector was an ECD (^{63}Ni 370 MBq, 10 mCi; cell current, 0.05 nA). In the GC program, the initial temperature of the column was 205 °C (220 kPa). Respective temperatures of the injection port and the detector were 230 °C and 250 °C.

3. Results and discussion

We began our investigation with six identical samples. The first one was submitted alone to MDP in a Retsch PM-100 ball mill, while the 2nd, 3rd, 4th and 5th portions were likewise subsequently submitted to MDP, using as additives metallic Ca, Al, CaO, respectively a 1:1 mixture of Ca and CaO. The last sample was mechanochemically treated with metallic Ca and extracted with a 1:1 mixture of *n*-propanol and toluene, under ultrasonication, for 3 h.

Thus, without any prior treatment, the first sample, consisting of 10.0 g of fly ash with 1.4% determined level of humidity, was submitted to ball-milling. Starting from a sample with an average value of 4000 TEQ pg g^{-1}, we observed an increase of this value, total toxicity becoming, after treatment, 5200 TEQ pg g^{-1}. This experiment was repeated three times, all attempts giving similar results. These results corroborated some of our unpublished previous researches, when we observed that some of the less toxic compounds tend to transform in more toxic (and subsequently more resistant toward hydrodechlorination) congeners. This tendency is confirmed by literature data. For example, octachlorodibenzodioxin (OCDD), which has a TEF of 0.0003 (van den Berg et al., 2006) can easily be hydrodechlorinated to tetrachlorodibenzodioxin (TCDD), which has a TEF of 1 (van den Berg et al., 2006) and is more resistant toward hydrodechlorination (Huang et al., 1996; Lynam et al., 1998). Indeed, it has been shown that the reactivity and isomer-specific dechlorination pathways of mono- to octachlorinated dioxin congeners could be described by quantum–mechanical parameters such as carbon charges and the magnitude of the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), whereby a smaller gap (which signifies greater molecular reactivity) was associated with higher chlorinated congeners (Huang et al., 1996; Lynam et al., 1998).

When metallic calcium was added as an additive in sample 2, no significant hydrodechlorination occurred. Instead, a slight increase of the TEQ was recorded (Table 1).

From these detailed data, the decrease of OCDD/OCDF concentrations and the slower decrease of lower-chlorinated PCDFs concentrations or even the increase of lower-chlorinated PCDDs concentrations are obvious.

Table 1
Direct MDP of fly ash samples without/with calcium.

PCDD/Fs + co-PCBs	DXNs init.[c]	Mechanochemical treatment[a]			
		Without added Ca		With added Ca[b]	
		Final[c]	Decomp. (%)[d]	Final[c]	Decomp. (%)[d]
2,3,7,8-TetraCDD	200	360	−80	70	65.0
1,2,3,7,8-PentaCDD	360	1800	−400	890	−147.2
1,2,3,4,7,8-HexaCDD	890	1200	−34.8	830	6.4
1,2,3,6,7,8-HexaCDD	2900	4100	−41.4	3100	−6.9
1,2,3,7,8,9-HexaCDD	1900	3000	−57.9	2300	−21.1
1,2,3,4,6,7,8-HeptaCDD	18 000	25 000	−38.9	26 000	−44.4
1,2,3,4,6,7,8,9-OctaCDD	41 000	29 000	29.3	41 000	0
2,3,7,8-TetraCDF	1100	670	39.1	590	46.4
1,2,3,7,8-PentaCDF	1800	1600	11.1	1900	−5.6
2,3,4,7,8-PentaCDF	3000	2200	26.7	3000	0
1,2,3,4,7,8-HexaCDF	1800	1200	33.3	1500	16.7
1,2,3,6,7,8-HexaCDF	2200	1900	13.6	2200	0
1,2,3,7,8,9-HexaCDF	880	540	38.6	610	30.7
2,3,4,6,7,8-HexaCDF	3600	2400	33.3	3100	13.9
1,2,3,4,6,7,8-HeptaCDF	4400	4700	−6.8	6000	−36.4
1,2,3,4,7,8,9-HeptaCDF	690	900	−30.4	1100	−59.4
1,2,3,4,6,7,8,9-OctaCDF	5600	2900	48.2	5400	3.6
Total (PCDDs + PCDFs + co-PCBs)	360 000	460 000	−27.8	410 000	−13.9
Total TEQ (pg TEQ g^{-1})	4000	5200	−30.0	4400	−10.0

[a] GC–ECD analysis, 400 rpm, 20 h.
[b] Ca/ash = 0.1 g/10 g, balls ($\varnothing$ = 10 mm, 10 pieces).
[c] pg g^{-1} total treated ash.
[d] Percentage, minus ("−") means increase.

When no additive is added and fly ash is directly submitted to the ball-milling process (previously to washing), the TEQ tends to grow (from 4000 pg g^{-1} up to 5200 pg g^{-1}) – entry 1 in both Tables 1 and 2. We assumed that this process is due to the transformation of highly chlorinated (octa-, hepta-) derivatives (with lower TEFs) into medium chlorinated derivatives (tetra-, penta-) with higher TEF, probably under the influence of some of the mineral components of the fly ash. Therefore, we decided to try its removal by simple washing, operation that we performed under ultrasonication. Coincidentally, the TEQ of washed samples presented the same value of 5200 pg g^{-1}: we had to assume that the same process occurred during ultrasonication, the ultrasound activation playing a similar role than mechanochemical activation, in the braking of less energetic C–Cl bonds in the OCDD/Fs. The severed chlorine are probably transformed into water-soluble inorganic forms. The presence of chlorine in the aqueous phase was determined through Mohr's titration. Since ultrasonication in water is a simple method for the elimination of a certain percentage of the chlorine, we decided to thoroughly wash each sample before ball-milling it. Thus, all initial samples introduced in the ball-milling process showed a 5200 TEQ pg g^{-1} initial concentration (instead of 4000 pg g^{-1} before washing). We did not find this detrimental for our research: indeed, the PCDDs, PCDFs and PCBs congeners now present in the fly ash mixture are of the more toxic nature and more resistant toward hydrodechlorination. The success of the decontamination procedure would be therefore more significant.

Our next step was to add various additives to these washed samples: metallic Ca, CaO, metallic Al and a mixture 1:1 of metallic Ca and CaO. The results are summarized in Table 2.

The relatively low degradation yield recorded when using only CaO (entry 2) is somehow in accordance with previous results reported by Yan et al. (2007). On the other hand, the use of only metallic Ca (it was introduced in the ball mill as purchased, with particle size 0.1–2 mm, without any preliminary treatment) did not prove to be as successful as expected (entry 3). Nevertheless, compared to the use of another metal, Al, metallic Ca was sensibly more effective. Finally, the combination of metallic Ca and CaO (entry 5) was the most effective, when no traces of chlorinated compound could be detected.

In order to assess the effectiveness of this procedure for future industrial application, we compared its detoxification yield with the one for a regular procedure actually applied. Such a classic approach usually implies a combination of extraction of chlorinated contaminants in an organic solvent and a thermal or chemical dechlorination process (EPA, 1994).

Thus, result obtained in entry 3 can be improved if an extraction is subsequently performed. Indeed, by simply washing with a 1:1

Table 2
MDP of washed fly ash samples.

Entry	Starting materials		Results (TEQ pg g^{-1})		Degradation yield (%)
	Fly ash (g)	Additive (g)	Initial TEQ	Final TEQ	
1[a]	10.0	–	4000	5200	–
2	10.0	CaO (0.01)	5200	2900	44.2
3	10.0	Ca (0.01)	5200	900	82.7
4	10.0	Al (0.01)	5200	3300	36.5
5	10.0	Ca + CaO (0.005 + 0.005)	5200	Undetectable	100
6[b]	10.0	Ca (0.01)	5200	79	98.5

[a] Initial sample, prior to water-washing.
[b] After the mechanochemical treatment, a 3 h extraction with n-PrOH: toluene (1:1) was performed.

mixture n-PrOH – toluene, the TEQ values of the already treated fly ash sample 3 are dropping from 900 pg g^{-1} to only 79 pg g^{-1}. Among the solvents we tested (ethanol, n-propanol, toluene), this mixture gave the best results. This proves that in the case of MDP with a single additive, an almost total degradation can be achieved, only if an extraction is performed after ball-milling. In the same time, a mixture of two additives insures a complete hydrodechlorination.

Table 3 presents detailed results obtained when using Ca only, respectively the mixture Ca–CaO. It is obvious that the last is the most effective, no chlorinated derivatives being detected (if present, these compounds were in concentration below the minimal limit of detection of the standard GC–ECD method used (JIS, 1999a,b)).

According to the theory of MDP (Beyer and Clausen-Schaumann, 2005), such processes take place in a triboplasma state (Heineke, 1984), a state in which free electrons can be easily generated by a so-called tribo-emission phenomenon (Nakayama, 2006). Materials have been organized in tribo-electric series (Gady et al., 1998; Ohara, 2003), in which they are ranging from most positive (tendency to lose electrons) to most negative (tendency to gain electrons). Such an efficient materials for triboemission of electrons, found in these tables, are sand, glass or quartz (Hasegawa et al., 1995), which

explains the excellent results obtained previously for the hydrode-chlorination of PCBs (Zhang et al., 2001; Nomura et al., 2005; Wei et al., 2009). Thus, assuming that the hydrodechlorination MDP occurs in a triboplasma state, subsequent to a triboemission of electrons, our results would fit in this scheme in the following manner:

- steel is in a triboseries just below the "neutral" cotton, thus the collision of steel balls will generate only heat (no tribo-emission) – only limited hydrodechlorination would take place, only for those species who can easily eliminate the chlorine atom (entry 1), $e.g.$ the higher chlorinated congeners, yielding mostly tetra- or pentachlorinated dioxins, with a higher TEF (van den Berg et al., 2006);
- for his part, aluminum is the first metal placed in such a tribo-series higher than cotton, with limited tribo-plasma generation; however it will allow a certain ratio of hydrodechlorination (entry 4) along with a small decrease of the TEQ;
- Ca and calcite (CaCO$_3$) are above Al, thus they generate higher tribo-plasma fields and should therefore provide better results, expressed as a more significant TEQ decrease (entries 2 and 3). Finally, the mixture CaO/Ca offered excellent MDP results, implying a cumulation as well as a possible synergic effect

Table 3
MDP of washed fly ash with Ca and Ca/CaO mixture.

| PCDD/Fs + co-PCBs	DXNs init.[c]	MDP treatment[a]			
		Ca additive[b]		Ca/CaO additive	
		Final[c]	Decomp. (%)[d]	Final[e]	Decomp. (%)[d]
2,3,7,8-TetraCDD	170	79	58.5	<5	100
1,2,3,7,8-PentaCDD	1000	350	65.0	<5	100
1,2,3,4,7,8-HexaCDD	1100	250	77.3	<10	100
1,2,3,6,7,8-HexaCDD	4000	570	85.8	<10	100
1,2,3,7,8,9-HexaCDD	2900	410	85.9	<10	100
1,2,3,4,6,7,8-HeptaCDD	33 000	3100	90.6	<20	100
1,2,3,4,6,7,8,9-OctaCDD	48 000	3000	93.8	<100	100
2,3,7,8-TetraCDF	730	180	75.3	<5	100
1,2,3,7,8-PentaCDF	2100	260	87.6	<5	100
2,3,4,7,8-PentaCDF	3200	370	88.4	<5	100
1,2,3,4,7,8-HexaCDF	1700	180	89.4	<10	100
1,2,3,6,7,8-HexaCDF	2600	270	89.6	<10	100
1,2,3,7,8,9-HexaCDF	740	110	85.1	<10	100
2,3,4,6,7,8-HexaCDF	3700	290	92.2	<10	100
1,2,3,4,6,7,8-HeptaCDF	9000	680	92.4	<20	100
1,2,3,4,7,8,9-HeptaCDF	1400	130	90.7	<20	100
1,2,3,4,6,7,8,9-OctaCDF	8800	450	94.9	<100	100
Total(PCDDs + PCDFs + co-PCBs)	580 000	67 000	88.4	–	100
Total TEQ (pg TEQ g^{-1})	5200	900	82.7	–	100

[a] GC–ECD analysis, 400 rpm, 20 h.
[b] Ca/ash = 0.1 g/10 g.
[c] pg g^{-1} total treated ash.
[d] Percentage.
[e] Minimal limit of detection of the JIS standard method used, in pg g^{-1}.
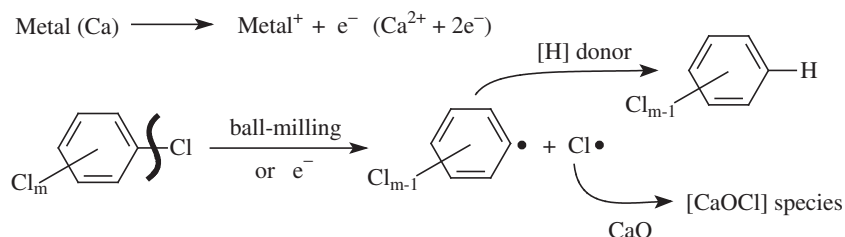
Scheme 1. Possible radicalic dechlorination pathway.

between the two species (entry 5). Since both methodologies (the use metallic calcium in an alcoholic hydrodechlorination process, respectively the mechanochemical dechlorination with calcium oxide) have proved their efficiency in the treatment of various substrates, fly ash included, it is not surprising that the mixture of both reagents is effective in a MDP applied to fly ash. What could be surprising is the amplitude of the hydrodechlorination: no traces of any chlorinated compound was recorded. Literature data (Ma et al., 2005) demonstrated synergic effect of commercial CaO and a-Fe$_2$O$_3$ in the thermal dechlorination of hexachlorobenzene. Indeed, when CaO and alpha-Fe$_2$O$_3$ coexisted, HCB was dechlorinated by about 98% after 0.5 h reaction at 300 degrees C. A similar synergic effect can be the explanation for the remarkable results obtained with a mixture of CaO and metallic Ca.

Indeed, assuming a radicalic hydrodechlorination process (Mitoma et al., 2009b), metallic calcium is more prone to generate free electrons than its oxide which, in return, is available for the trapping of chlorine atoms formed in the process (Ikoma et al., 2001; van der Heijden et al., 2005) (Scheme 1).

4. Conclusion

The mechanochemical treatment of contaminated fly ash with PCDDs, PCDFs and PCBs in the presence of a mixture of metallic calcium and CaO is the most effective, since dechlorination is total – no traces of chlorinated compound was detected after the treatment of a sample presenting a previously determined TEQ of 5200 pg g^{-1}. Such a process could represent the future in terms of sustainable development and ecofriendly depolluting techniques: it does not require heating, organic solvents, fancy catalysts or expensive reagents, it does not yield harmful by-products, it does not generate exhaust gases. On the contrary, it requires only electricity, cheap and commercially available reagents and eventually water.

References

Aresta, M., Dibenedetto, A., Pastore, T., 2005. Mechanochemistry: an old technology with new applications to environmental issues. Decontamination of polychlorobiphenyl-contaminated soil by high-energy milling in the solid state with ternary hydrides. In: Lichtfouse, E., Schwarzbauer, J., Robert, D. (Eds.), Environmental Chemistry. Springer, New York, pp. 553–559.

Beyer, M.K., Clausen-Schaumann, H., 2005. Mechanochemistry: the mechanical activation of covalent bonds. Chem. Rev. 105, 2921–2948.

Birke, V., Mattik, J., Runne, D., 2004. Mechanochemical reductive dehalogenation of hazardous polyhalogenated contaminants. J. Mater. Sci. 39, 5111–5116.

EPA Report, 1994. EPA Terra-Kleen Solvent Extraction Technology. EPA Report Number EPA/540/MR-94/521.

Gady, B., Reifenberger, R., Rimai, D.S., 1998. Contact electrification studies using atomic force microscope techniques. J. Appl. Phys. 84, 319–322.

Hall, A.K., Harrowfield, J.M., Reinhold, R.J., McCormick, P.G., 1996. Mechanochemical reaction of DDT with calcium oxide. Environ. Sci. Technol. 30, 3401–3407.

Hasegawa, M., Ogata, T., Sato, M., 1995. Mechano-radicals produced from ground quartz and quartz glass. Powder Technol. 85, 269–274.

Heineke, G., 1984. Tribochemistry. Carl Hanser Publishing, Berlin.

Huang, C.L., Harrison, B.K., Madura, J., Dolfing, J., 1996. Gibbs free energies of formation of PCDDs: evaluation of estimation methods and application for predicting dehalogenation pathways. Environ. Toxicol. Chem. 15, 824–836.

Ikoma, T., Zhang, Q., Saito, F., Akiyama, K., Tero-Kubota, S., Kato, T., 2001. Radicals in the mechanochemical dechlorination of hazardous organochlorine compounds using CaO nanoparticles. Bull. Chem. Soc. Jpn. 74, 2303–2309.

Inoue, T., Miyazaki, M., Kamitani, M., Kano, J., Saito, F., 2004. Mechanochemical dechlorination of polyvinyl chloride by co-grinding with various metal oxides. Adv. Powder Technol. 15, 215–225.

JIS K 0311-1999a. Method for Determination of Tetra-through Octa-chlorodibenzo-*p*-dioxins, Tetra-through Octa-chloro-Dibenzofurans and Coplanar Polychlorobiphenyls in Stationary Source Emissions. Japanese Industrial Standard Committee, Tokyo.

JIS K 0312-1999b. Method for Determination of Tetra-through Octa-chlorodibenzo-*p*-dioxins, Tetra-through octa-chloro-dibenzofurans and Co-planar Polychlorobiphenyls in Industrial Water and Waste Water. Japanese Industrial Standard Committee, Tokyo.

Loiselle, S., Branca, M., Mules, G., Cocco, G., 1997. Selective mechanochemical dehalogenation of chlorobenzenes over calcium hydrides. Environ. Sci. Technol. 31, 261–265.

Lynam, M.M., Kuty, M., Damborsky, J., Koca, J., Adriaens, P., 1998. Molecular orbital calculations to describe microbial reductive dechlorination of polychlorinated dioxins. Environ. Toxicol. Chem. 17, 988–997.

Ma, X., Zheng, M., Liu, W., Qian, Y., Zhao, X., Zhang, B., 2005. Synergic effect of calcium oxide and iron (III) oxide on the dechlorination of hexachlorobenzene. Chemosphere 60 (6), 796–801.

Mio, H., Saeki, S., Kano, J., Saito, F., 2002. Estimation of mechanochemical dechlorination rate of poly(vinyl chloride). Environ. Sci. Technol. 36, 1344–1348.

Mitoma, Y., Nagashima, S., Simion, C., Simion, A.M., Yamada, T., Mimura, K., Ishimoto, K., Tashiro, M., 2001. Dehalogenation of aromatic halides using metallic calcium in ethanol. Environ. Sci. Technol. 35, 4145–4148.

Mitoma, Y., Uda, T., Egashira, N., Simion, C., Tashiro, H., Tashiro, M., Fan, X., 2004. Approach to highly efficient dechlorination of PCDDs, PCDFs, and coplanar PCBs using metallic calcium in ethanol under atmospheric pressure at room temperature. Environ. Sci. Technol. 38, 1216–1220.

Mitoma, Y., Takase, M., Yoshino, Y., Masuda, T., Tashiro, H., Egashira, N., Oki, T., 2006. Novel mild hydrodechlorination of PCDDs, PCDFs, and co-PCBs inside fly ash using a calcium-promoted rhodium carbon catalyst in methanol. Environ. Chem. 38, 215–218.

Mitoma, Y., Egashira, N., Simion, C., 2009a. Highly effective degradation of polychlorinated biphenyls in soil mediated by a Ca/Rh bicatalytic system. Chemosphere 74, 968–973.

Mitoma, Y., Kakeda, M., Simion, A.M., Egashira, N., Simion, C., 2009b. Metallic Ca−Rh/C-methanol, a high-performing system for the hydrodechlorination/ring reduction of mono- and poly chlorinated aromatic substrates. Environ. Sci. Technol. 43, 5952–5958.

Monagheddu, M., Mulas, G., Doppiu, S., Cocco, G., Racanelli, S., 1999. The reduction of polychlorinated dibenzo-dioxins and dibenzofurans in contaminated muds by mechanically induced combustion reactions. Environ. Sci. Technol. 33, 2485–2488.

Nakayama, K., 2006. Microplasma generated in a gap of sliding contact. J. Vac. Soc. Jpn. 49, 610–623.

Noma, Y., 2002. Radicalplanet Technology (Mechanochemical Principle). In Japanese Pesticides Treatment Fact Sheets.

Nomura, Y., Nakai, S., Hosomi, M., 2005. Elucidation of degradation mechanism of dioxins during mechanochemical treatment. Environ. Sci. Technol. 39, 3799–3804.

Ohara, K., 2003. Relationship between triboelectric series of atomic groups and dipole moment of the atomic groups which combine with linear hydrocarbon chain. In: Proceedings of the 7th International Conference on Properties and Applications of Dielectric Materials, vol. 3, pp. 1047–1050.

Tanaka, Y., Zhang, Q., Saito, F., 2003. Mechanochemical dechlorination of trichlorobenzene on oxide surfaces. J. Phys. Chem. B 107, 11091–11097.

Tongamp, W., Kano, J., Zhang, Q., Saito, F., 2008. Simultaneous treatment of PVC and oyster-shell wastes by mechanochemical means. Waste Manage. 28, 484–488.

Van den Berg, M., Birnbaum, L.S., Denison, M., DeVito, M.J., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006. The 2005 World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol. Sci. 93, 223–241.

Van der Heijden, A.W.A.M., Belliere, V., Espinosa Alonso, L., Daturi, M., Manoilova, O.V., Weckhuysen, B.M., 2005. Destructive adsorption of CCl$_4$ over Lanthanum-based solids: linking activity to acid–base properties. J. Phys. Chem. B 109, 23993–24001.

Vijgen, J., 2002. New and emerging techniques for the destruction and treatment of pesticides wastes and contaminated soils: mechanochemical dehalogenation. In: Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III), NATO/CCMS Pilot Study, International HCH and Pesticides Association, Fellowship Report.

Wei, Y., Yan, J., Lu, S., Li, X., 2009. Mechanochemical decomposition of pentachlorophenol by ball milling. J. Environ. Sci. 21, 1761–1768.

Yan, J.H., Peng, Z., Lu, S.Y., Li, X.D., Ni, M.J., Cen, K.F., Dai, H.F., 2007. Degradation of PCDD/Fs by mechanochemical treatment of fly ash from medical waste incineration. J. Hazard. Mater. 147, 652–657.

Zhang, Q., Saito, F., Ikoma, T., Tero-Kubota, S., Hatakeda, K., 2001. Effects of quartz addition on the mechanochemical dechlorination of chlorobiphenyl by using CaO. Environ. Sci. Technol. 35, 4933–4935.