

## DETOXIFICATION OF POPs WASTES, DIOXIN, PCB AND AGRICULTURAL CHEMICALS BY MECHANOCHEMICAL PRINCIPLE

Shimme K<sup>1</sup>, Takase K<sup>2</sup>, Deguchi Y<sup>3</sup>, Okawa A<sup>1</sup>, Mizuno M<sup>2</sup>, Saito F<sup>4</sup>, Kano J<sup>4</sup>,

<sup>1</sup>Radicalplanet Research Institute Ltd., Nagoya, 465-0095 Japan; <sup>2</sup>Smitomo Heavy Industries Techno-Fort Ltd., Niihama, 792-8588 Japan; <sup>3</sup>Kaneka Techno Research Ltd., Settsu, 566-0072 Japan; <sup>4</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 980-8577 Japan;

### Abstract

Radicalplanet Technique is the complete detoxification technology that changes POPs wastes, chlorinated organic compounds, into safety compounds under non-heating, atmospheric conditions and closed system by using of the mechanochemical principle. While the Pesticides, Dioxin, PCB, and related POPs wastes are treated, there are neither exhaust gas nor effluents at all. There is no fear of secondary pollution and this process is guaranteed clean conditions. When the physical energy is exerted greater than a specific strength, the organic chlorinated compounds will be chemically activated. The bond of each molecule is cut by mechanical energy and decomposed into the activated state, called the radical state, after then chemical reaction is accelerated. Safe and less expensive additives, such as CaO, are selected in this treatment. After detoxification treatment, the value of toxic equivalent became below 1pg-TEQ/g. The destruction removal efficiency was over the 99.9999%. The chlorines combined with CaO-radical and formed chlorinated inorganic stable compounds, such as Ca(OH)Cl, CaCl<sub>2</sub>, It is confirmed that the final product is quite safety by method of Bioassay valuation. This radicalplanet technique was officially granted in April 1, 2004, in Japan.

### Introduction

Recently it is widely recognized that the chemical reaction occurred by the mechanochemical principle.<sup>1</sup> We paid attention to some reports that the man-made negative legacy could be detoxified safely and completely. We constructed the practical machine that is the type of planetary ball mill and proved the chemical reactions that the chlorine changed from organic compounds to inorganic materials, that is to say, harmful chloride compounds converted into safety inorganic materials by using this practical machine. As the target organic compounds, the soil and ash polluted by dioxins<sup>2, 3</sup>, PCB oil and stabilizer contaminated by PCB and POPs wastes (BHC, Chlordane, Endrin, etc.) were selected. On the practical machine, all these organic compounds were decomposed to harmless inorganic materials whose toxicity of dioxins became less than 10pg-TEQ/g, safety values.

### Experimental Method

Experiments were carried out in a practical-scale planetary ball mill holding three vessels (each capacity is 250L) contained steel balls. Figure 1 shows the schematic profile of the pilot-scale E-200 type system. The each rotational speed, three reaction bawls and base, was 70 rpm (~100 rpm: practical use), conversely and constantly during the detoxification reaction.

1. Dioxin (Polluted soil and ash): The toxic equivalent of dioxins contained in the polluted soil was 7500 pg-TEQ/g, and that of dioxins contained in the fly ash was 6900 pg-TEQ/g. The soil and ash were put in the thick-paper bags.

2. PCB: The PCB (53.6%PCB+38.4%Trichloro-Benzene) in the bottles, and some stabilizers contained PCB were treated by using the dechlorination agent, CaO (burnt lime). PCB oil was put in the glass bottles and stabilizers containing PCB were put as these are.

3. Agricultural Chemical: The agricultural Chemicals contained BHC (5%BHC), Chlordane (42%), DDT (5%), Endrin (2%) and PCNB (20%) were treated with the dechlorination agent. Agricultural chemicals were put in the vinyl bags or in the glass bottles.

Table 1 shows the distribution ratio of the dechlorination agent to the polluted soil and ash, to the PCB Oil and stabilizers and to the agricultural chemicals. The distribution value was decided by the condition of test. In the case of measuring the limitation value, the distribution ratio was increased to high level.



Fig. 1 Schematic Profile of E-200

Table 1 Distribution Ratio of Detoxification Agent (Lime or B.F. Slag)

	Dechlorination Agent / Target (weight)	
	Experimental Distribution Ratio	Suitable Distribution Ratio
Aim	Limitation(Final Value) Measurement	Practical Treatment
Dioxin / Soil*	4~6/1	3/1
/Ash*	4~6/1	3/1
PCB /9.6%PCB	25/1	12/1
/0.8%PCB	12/1	6/1
/Stabilizer	6/1	3/1
Agricultural Chem.*	3~12/1	3/1

\*:Lime/B.F.Slag=2/1

Table 2 Composition of Lime and Blast Furnace Slag

	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO
Lime	95.1	0.9	0.8	1.4
B.F. Slag	42.4	33	14.5	6.5

In order to decide the suitable ratio, the some samples were taken out during the treatment period, and we selected the most suitable distribution ratio. The dechlorination agent were burnt lime and blast furnace slag and those contents are shown in Table 2. In these experiments, samples were evaluated toxic equivalent by the concentration of dioxins and Co-PCB. The analysis is according to "Soil Investigation Tentative Manual that affects Dioxins"(release from Environment Agency) and "Manual of Method for Determining Toxic Matters caused by Atmospheric Pollution"(release from Environment Agency). In addition, Toxicity Equivalency Factors (TEQ) is according to WHO-TEF (1997).

**Experimental Results and Discussions**

(1) Detoxification reaction

The behaviors of the toxic equivalent during the rotational period are shown in Fig.2 (Soil Polluted by dioxin), Fig.3 (51.3%PCB+38.4%Trichloro-Benzene) and Fig.4 (3%BHC emulsion) respectively.<sup>5</sup> It was found that the dioxin toxic equivalent decreased with the increase of the grinding (chemical reaction) time in each case. After about 5 hours, the dioxin TEQ decreased less than 10pg-TEQ/g (the analytical limitation, non detected level, is about 10pg/g). After 8 hours, the toxicity of Co-PCB reduced less than 0.01pg-TEQ/g. Dechlorination ratio reached above 99.9999% in the treatment of target compounds and organic-chlorine compound was never detected. As the result of investigating these data, it was estimated that the decomposing speed will be increased twice and that the detoxification time will be reduced by half with increasing the rotational speed (in case of 100rpm). However the decomposing speed will be decrease with increasing the amount of target and the concentration of target, as shown in PCB and BHC, the dechlorination reaction proceeds rapidly and reaches less than the analytical limitation.

In the practical process, it is very important that the suitable practical conditions should be chosen, a rotational speed, steel ball conditions, an amount of target, a concentration of target, a ratio of CaO and so on.

Usually the toxicity of dioxin is presented by the toxic equivalent. Coefficient of the toxic equivalent is shown in each

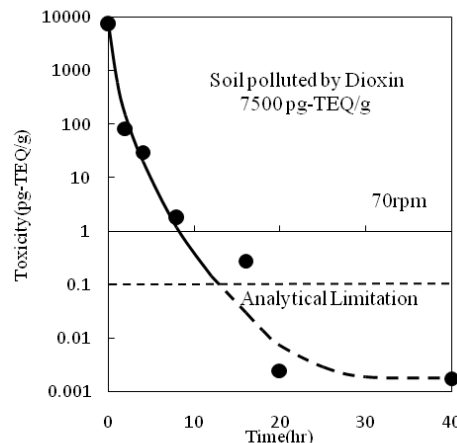


Fig.2 Behaviour of Toxicity (Soil polluted by Dioxin)

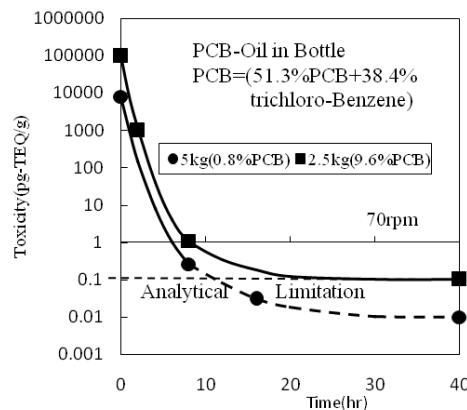


Fig.3 Behaviour of Toxicity (51.3%PCB-Oil)

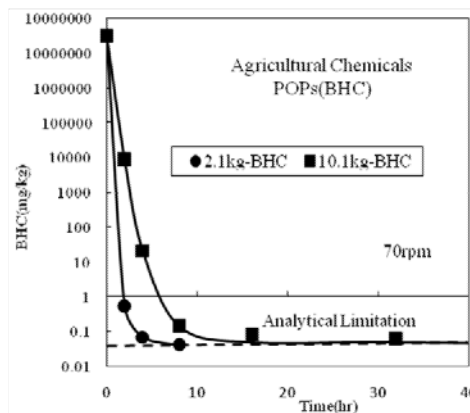


Fig.4 Decomposition of Agricultural Chemicals(BHC)

isomer of dioxins. In the detoxification reaction of the PCNB, an interesting result was observed that the contents of PCNB (or HCB) decreased exponentially but the toxic equivalent value increased only slightly in the initial stage of the detoxification reaction and after then the equivalent value decreased exponentially, shown in Fig.5. This phenomenon observed in early period of dechlorination reaction was estimated to depend on the difference of the reaction speed on the PCNB-isomers and Dioxin-isomers.<sup>3</sup>

## (2) By-Product

### (a) Safety

As the dioxin toxic equivalent of the soil and ash become less than 10pg-TEQ/g after treatment of this process, the powdered soil is both safety and is able to reuse for high strength and hard materials after solidifying the powdered soil with water.<sup>3</sup>

### (b) Reaction Mechanism in PCB Destruction.<sup>4,6</sup>

As all of the organic chlorine of PCB become to inorganic chlorine after treatment of this process, the organic chloride-compounds can be dissolved out from the powdered by-product with a normal suitable solvent. It was confirmed that the organic compounds were constituted from the hydrogen-reduction of Biphenyl, Terphenyl, Quarterphenyl, and lower molecular hydrocarbon (alkane, alken, benzene, toluene and lower molecular poly-cyclic aromatic hydrocarbons).<sup>4,6</sup> The results of the more detailed analysis, we are convinced that the ring of benzene was cut to the separated state and became to the radical state.

GC/MS-SCAN: Toluene, Styrene and some kinds of esters were observed by extracting with Ethyl acetate. Benzene, Ethyl dimethyl benzene and some kinds of aldehyde were observed by extracting with toluene.

GPC: The molecular weight of organic compounds extracted with Ethyl acetate or Toluene were in the region of 1400 ~ 200 by converting into the polystyrene molecular weight. The strong peak was 269 at the instruction with Ethyl acetate and was 168 at the instruction with Toluene. The molecular weight decreased to the region of 64 ~ 596 by extracting with Toluene after washing the sample by nitric acid, and the amount of extracted compounds decreased with proceeding of the chemical reaction.

GT-DTA: The existence of the free carbon was confirmed in the remnant, which remained after washing by nitric acid and extracting with Toluene. The free carbon was estimated an inorganic compound. The weight of free carbon was calculated, a few percent, by the weight loss in burning at the atmospheric condition, after burning at the nitrogen condition. The amount of the free carbon increased with proceeding of that reaction.

IR: The absorption peaks originated in carbon hydrate were observed in the region of 2920  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$ , those in aromatic compounds were 1520  $\text{cm}^{-1}$  and 760  $\text{cm}^{-1}$  and that in fatty acid was 1700  $\text{cm}^{-1}$ .

NMR: The absorption peaks originated in proton of carbon hydrate residue were observed in the region of 0.9ppm, 1.3ppm and that originated in proton of aromatic compounds was observed in 6.7 ~ 7.2ppm.

GC/MS (Gas contents): The methane, ethane and benzene were observed in the vessels during the chemical reaction. The amount of these gases decreased with proceeding of the chemical reaction and these gases were never observed at the end of reaction. It was estimated that these gases were absorbed and combined with the

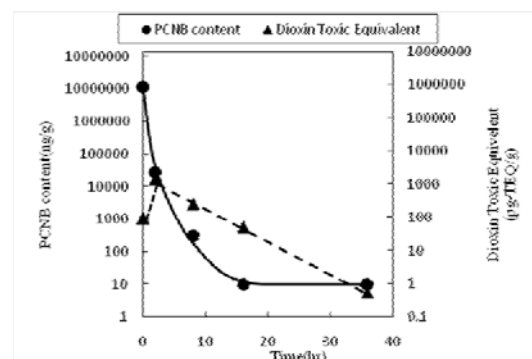


Fig.5 Decomposition of PCNB (Content and Dioxin Toxic Equivalent)

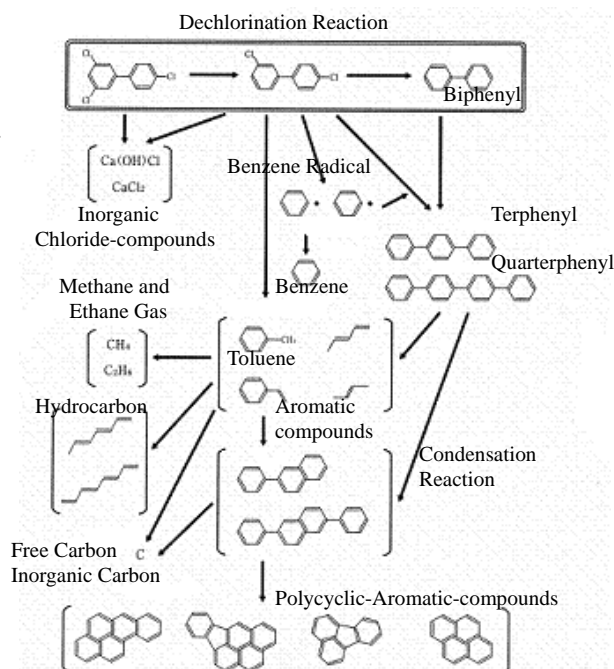


Fig.6 Estimation of PCB Destruction Mechanism

great fine powdered particles.

On these detail analytical data, the decomposition reaction mechanism was estimated and shown in Fig. 6.

As concerning of lower molecular poly-hydrocarbons, we confirmed that the organic compound is completely safe both by the toxic equivalent value and by the method of DR-CALUX (Bioassay valuation). Figure 7 shows that these values have a good coefficient of correlation. Then the by-product of PCB treatment is safety by the evaluation of PCB-TEQ (pg-TEQ/g). By the way, the inorganic-chlorine compounds in the by-product can be dissolved out with the water and become to safety salt water-solution. The powdered solid of by-product can be reuse for useful materials after solidifying with water, in much the same way as by-product of the soil and ash treatment.

### (3) Practical Use

From the above experimental results and the estimated dechlorination mechanism, it is realized that the mechanochemical process, called to "Radicalplanet technology" in Japan, is a quite effective method for detoxifying the soil and ash polluted by dioxins, the PCB Oil and wastes contained PCB and agricultural chemicals called POPs. This technology is new non-combustion technology, is suitable for admixture of POPs wastes and is officially granted by the notification in Japan.

As the admixture of the POPs wastes, there are concrete brocks, soil, glass, metal (cans and pipes), plastic masks, clothe, work gloves, protective clothing (tyvex), chipped wood, cardboard paper, pieces of plastic goods PP, PVC and liquid or emulsion in the bottle, such as oil and organic compounds. Both burnt lime and blast furnace slag are quite effective dechlorination agent and low cost. In future, the non-combustion process will be an alternative destruction technology of incineration. In order to accelerate the chemical reaction speed, the authors had better to increase the rotational speed of Machine and to supply something into the vessels. It is possible to shorten the detoxification time to one quarter by increasing the rotational speed twice.

When the much wastes should be treated, such as soil, protective clothing and masks, the authors will recommend using one unit of equipment which is consisted of three machines, because these machines will be operated at high efficiency by shift, for example two operating by three machines. The safety is very important factor at the practical use. The polluted materials never expand, because this process is a closed system and never occur the exhaust gas and effluents during chemical reaction. The safety of this process will get the community and public acceptance. The authors recommend to using this Radicalplanet Process in order to treat in safety the soil and ash polluted by dioxins (10ng-TEQ/g), 1000 t/y per one unit of the equipment. On the case of PCB wastes (stabilizer), this process can be treat 500 t/y per one unit of the equipment. On the case of POPs wastes (with BHC content of 0.1%), this process can be treat 250-500 t/y per one unit of the equipment. The capacity of this process may be different from density of materials and the concentration of the pollution.

### Acknowledgements

The authors are grateful to Prof. Hosomi M, Tokyo University of Agriculture and Technology, for his leadership in the mechanochemical reaction mechanism. The help from Prof. Miyata H, Setsunan University, who directed some guidance in the practical use of this technology, is also gratefully acknowledged.

### References

1. Hall AK, Harrowfield JM, Hart RJ and McCormick PG. *Environmental Science & Technology* 1996;30:3401
2. Shimme K, Akazawa T, Matsuo T, Saito F, Kano J. *Resources Processing Society of Japan* 2001; 48:238
3. Shimme K, Akazawa T, Yamamoto H, Kano J, Saoto F. *World Congress on Particle Technology 4* 2002; 406
4. Shimme K, Deguchi Y. *Resources Processing Society of Japan* 2003; 50:209
5. Shimme K. *Environmental Solution Technology* 2005; 31:16
6. Shimme K, Takase K, Shiozaki K, Deguchi Y, Okawa A. In: *Sentan Funsai gijyutsu to ouyou*, Association of Powder Process Industry and Engineering, Japan (ed.), NGT Press, Tokyo, 2006:502

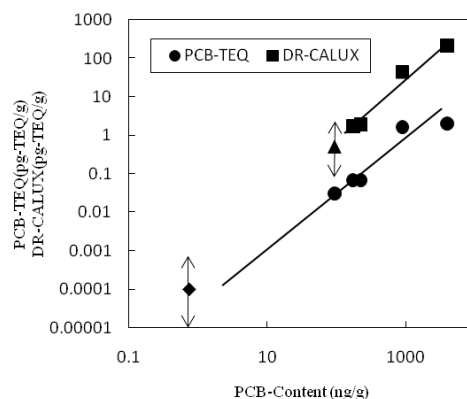


Fig. 7 Relation between -PCB Content and PCB-TEQ, DR-CALUX