

Chemical Degradation of Dieldrin using Ferric Sulfide and Iron Powder

Junko Hara, Yoshishige Kawabe, Takeshi Komai and Chihiro Inoue

Abstract—The chemical degradation of dieldrin in ferric sulfide and iron powder aqueous suspension was investigated in laboratory batch type experiments. To identify the reaction mechanism, reduced copper was used as reductant. More than 90% of dieldrin was degraded using both reaction systems after 29 days. Initial degradation rate of the pesticide using ferric sulfide was superior to that using iron powder. The reaction schemes were completely dissimilar even though the ferric ion plays an important role in both reaction systems. In the case of metallic iron powder, dieldrin undergoes partial dechlorination. This reaction proceeded by reductive hydrodechlorination with the generation of H^+ , which arise by oxidation of ferric iron. This reductive reaction was accelerated by reductant but mono-dechlorination intermediates were accumulated. On the other hand, oxidative degradation was observed in the reaction with ferric sulfide, and the stable chemical structure of dieldrin was decomposed into water-soluble intermediates. These reaction intermediates have no chemical structure of drin class. This dehalogenation reaction assumes to occur via the adsorbed hydroxyl radical generated on the surface of ferric sulfide.

Keywords—Dieldrin, kinetics, pesticide residue, soil remediation

I. INTRODUCTION

THE Persistent organic pollutions (POPs) such as organochlorine pesticides are synthetic chemicals that used mainly as pesticides since the middle of 1940s. Many countries have banned their usage in 1970s ~ 1980s due to their environmental persistence, bioaccumulation and characteristics of toxicity. Unfortunately, these chemicals have already spread worldwide and are even detected in several places [1]-[6]. Some developing countries are still using organochlorine pesticide for agricultural chemical because of low cost and versatility in controlling various insects. Most of these compounds are considered to act as environmental hormones, which disrupt reproductive cycles of humans and wildlife. Among them, aldrin and dieldrin are one of the most persistent chlorinated cyclodien pesticides in environment, and extremely

persist in agricultural fields for a long time. The cultivation of strictly absorbent crops is refrained voluntarily [6]. A common reaction that occurs in the environment is aldrin epoxidation to form the more persistent dieldrin.

Several remediation techniques: bioremediation, UV/Fenton, UV/chemical, solar photocatalytic technique, Pd/C catalyst have been reported, but most studies have shown the transformation of dieldrin to mono- or di- dechlorinated intermediates except Fenton technique [7]-[12]. In this study, we investigated the chemical dehalogenation of dieldrin using ferric sulfide and ferric iron powder. The transformation of dieldrin was assessed by monitoring its disappearance and products released with time. The chemical degradation mechanism and reaction kinetics were also discussed. Ferric iron powder has been practically used for in-situ dechlorination technique of volatile chlorinated ethylene [13]. Ferric sulfide was also reported to have dechlorination ability of chlorinated benzene and volatile chlorinated ethylenes [14]-[15]. Dieldrin is used for agricultural pesticide, so that in-situ remediation method using these powder is useful to treat extend over vast cultivated field, if they have a enough detoxification ability.

II. MATERIALS AND METHODS

A. Chemicals

Dieldrin[1,2,3,4,10,10-hexachloro-6,7,-epoxy-1,4,4a,5,6,7,8,8a-octahydro-exo-1,4,-endo-5,8-dimethanonaphthalene] used in this study was obtained from G.L.Science Co. Ltd. with 98 % purity. The other all chemicals except ferric iron and ferric sulfide were purchased from Wako Chemicals Co.. The solvents used in the experiment, including n-hexane and acetone, were residual agricultural chemical analysis graded. Reduced copper ($\phi=150\sim 250\mu m$) purchased from Wako Chemical Co. with 99.5% purity was used as reductant.

Ferric sulfide is natural pyrite obtained from Yanahara Mine in Okayama, Japan. The chemical composition of the used pyrite samples is given in Table 1. The composition was analyzed by EDX (EDX-700HS, Shimadzu Co. Ltd.). Main elements included iron and sulfur, and 4.4 wt% of minor elements, such as Zn, Cu and Si. The pyrite rock sample was ground with a ceramic mortar and pestle, further ground with a ceramic ball-mill and sieved. The fraction of 20 to 38 μm was retained for use. Prepared pyrite was rinsed several times with distilled water and ultrasonicated for 30 min to remove fine materials from surface. The specific surface areas of the treated pyrite measured using the BET method (NOVA 2000e, Yuasa Ionics Inc.) was 0.2 m^2/g .

Ferric iron powder was supplied by Dowa Iron Powder Co. Ltd., Japan (code number: E-200), which was produced by coke reduction of iron one and has been used commercially to treat

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wastewater contaminated mainly with volatile chlorinated organic compounds, e.g. PCE, TCE and DCE. The iron powder sample has a porous structure with a specific surface area of 3.9m²/g determined by BET analysis and included the impurities shown in Table 1.

Both powder samples were washed by 1M HNO₃ solution to remove the oxidized layer on the surface. They were then adequately rinsed by ultra pure water and then dehydrate in vacuum dryer.

B. Analytical procedures

Dehalogenation experiments were conducted in 100ml closed batch vials at room temperature. The vials were first filled with 10ml of Milli-Q grade ultra-pure water and deoxygenating using nitrogen gas stream to make anaerobic condition. 1g (±0.01g) of Ferric iron or ferric sulfide powder were then added, and were followed by deoxygenating if applicable and crimp-sealing with Teflon-liner septa and a cap. In addition, following condition vials also set to identify the reaction mechanism: 1g of reduced copper, 1g of ferric iron powder + 1g of reduced copper, 1g of ferric sulfide + 1g of reduced copper. Experiments were initiated by spiking with concentrated dieldrin solvents (in n-hexane solvent) using micro syringes to obtain 5ppm in the vials.

The aerobic conditions with different O₂ conditions (10, 50, 100, 300, 833μmol) were obtained by the injecting a predetermined volume of O₂ into the deoxygenated vials. The experiment with 833μmol is equilibrium with atmosphere in this experimental condition.

All vials were shaken at 250 rev/min by vortex shaker (SR-2DS, Taitec) in darkness to isolate from any possible effect of light, add to use of brown vials.

C. Chemical Analysis

Entire dieldrin involved in adsorbed one on mineral surface or vial bottle were extracted by acetone and hexane by usage of benzo-[a]-pyren as surrogate chemicals. The dissolved water in solvents was eliminated by anhydrous sodium sulfate. After passing through a GC-50 glass fiber filter (Advantec), finally solvent samples are concentrated to hexane using evaporator (Syncore®Analyst, Buchi L. AG). Then their concentrations were determined by GC-MS (GC-MS5973N; Agilent) with a column from G.L.Science Co. Ltd. (InterCap 5MS/Sil, 30m×0.25mm I.D., 0.25μm stationary phase thickness.) Non-aqueous reaction products were also determined by GC-MS. Aqueous reaction products was measured by a high performance liquid chromatograph (DX-500; DIONEX.) with Ionpac AS15 column after 0.2μm filtration, and aqueous chemicals are identified by GC-MS (GCMS-QP2010 plus+DI-2010, Shimadzu Co. Ltd.).

III. RESULTS AND DISCUSSION

A. Dechlorination of Dieldrin

1) Degradation Rate of Dieldrin

The experimental results in Figure 1 show the degradation of dieldrin under anaerobic condition with time. More than 90% of dieldrin was degraded using ferric iron or ferric sulfide after 29 days. The initial reaction rates are summarized in Table 2, which calculated by pseudo-first order degradation rate equation (1).

$$\frac{dC_{diel\text{drin}}}{dt} = -kC_{diel\text{drin}} \quad (1)$$

where $C_{diel\text{drin}}$ is the concentration of dieldrin at time t, k is the pseudo-first-order reaction rate constant. The pseudo-first-order reaction rate constant are estimated from the linear regression of $\ln(C_t/C_0)$ versus time, where the concentration of dieldrin at time t and initial.

Initial degradation rate of the dieldrin using ferric sulfide was superior to that using ferric iron powder. Furthermore, the degradation rate was accelerated by reductant in ferric iron powder condition, but that was decelerated under ferric sulfide.

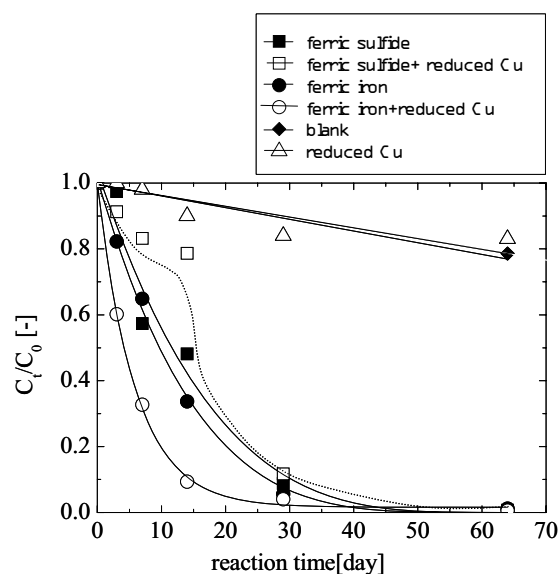


Fig. 1 Degradation of dieldrin by ferric sulfide, ferric powder with/without reduced copper. Evolution of the normalized remaining percentage of dieldrin with time.

Although the initial reaction rate was inferior to the other condition in the case of ferric sulfide with reductant, overall degradation ability was similar with the other conditions. The reaction schemes were assumed to be completely dissimilar even though the ferric ion plays an important role in both reaction systems.

Table II shows the solution pH of each reaction condition after 29days. In the case of ferric sulfide, the solution pH was feared to be acidic by sulfate ion. This is not suitable for in-situ remediation for agricultural field, but the acidification by ferric sulfide was buffered by reduced copper.

TABLE I
PSEUDO-FIRST-ORDER INITIAL RATE CONSTANT FOR DECHLORINATION OF DIELDRIN AND FINAL PH OF THE SOLUTION IN EACH CONDITION

Species	Ferric iron	Ferric iron + reduced Cu	Ferric sulfide	Ferric sulfide + reduced Cu
k	0.0882	0.1313	0.105	0.0192
pH	10.7	11.3	4.3	9.1

k: pseudo-first-order reaction rate constant of equation (1), pH denote the solution pH of water reacted after 29 days.

2) Effect of Oxygen

The effect of oxygen for dieldrin degradation with ferric sulfide

is estimated in here. Because we predicted that the degradation of dieldrin is the oxidation reaction between dieldrin and oxygen with heterogeneously catalyzed by a ferric sulfide, as reported in the TCE dehalogenation with ferric sulfide [15].

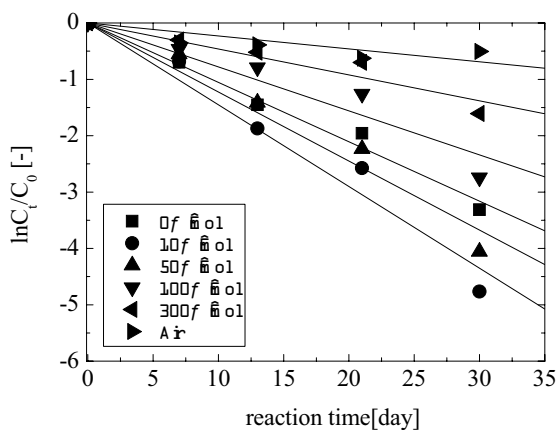
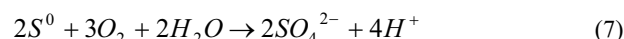
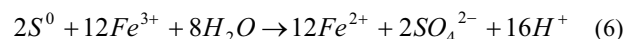
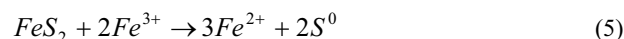
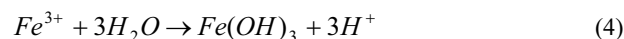
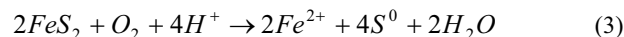
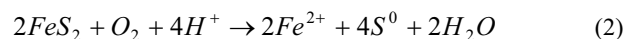


Fig. 2. Degradation of dieldrin by ferric sulfide under different oxygen condition (0, 10, 50, 100, 300, μmol). Evolution of the normalized remaining percentage of dieldrin with time.

Pseudo-first-order reaction rate constant for different oxygen vale were estimated by using equation (1). Each reaction rate had a good agreement with apparent first order reaction (Figure 2). The kinetic rates constant are summarized in Table. At the 10 μmol of oxygen injected one had a superior degradation rate. The reaction rate was not so decrease under aerobic condition, but decelerated rapidly by the increase of oxygen from 10 μmol.

This result did not assist the oxidation reaction between dieldrin and oxygen. Oxygen also acts as oxidant in oxidation of ferric sulfide. The oxidation mechanism of pyrite (which used as ferric sulfide in this research) has been reported [16]–[19], and oxidation of pyrite in aerobic condition are written as equation (2)–(7).



The existence of Fe^{2+} can catalyze the oxidation of pyrite. The oxidation rate of ferrous to ferric iron is higher under high Eh values [16]. The oxidation of pyrite is accelerated by the increment of oxygen, but it also decelerate degradation rate of dieldrin in our experimental system. It is assumed that cathodic reaction transfers electrons from surface of the pyrite to the aqueous oxidant species, such as O_2 and Fe^{3+} , and the electron could not use for dechlorination of dieldrin. The chemical activity of pyrite surface also decline by coating the oxidized layer in aerobic condition. In the low Eh condition, the oxidation cycle of pyrite (equation (2)-(7)) also proceed, but Fe^{2+} to Fe^{3+} and S^0 to SO_4^{2-} are declined. Considering form dechlorination kinetics of dieldrin proceeded in anaerobic and low Eh condition, O_2 is assumed to be not directly attacked the dieldrin, and controls the activity of pyrite surface.

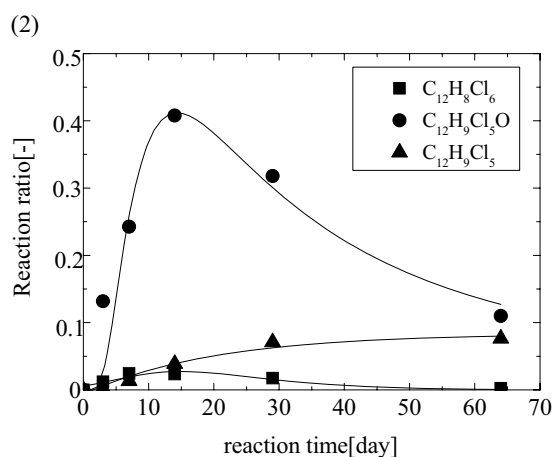
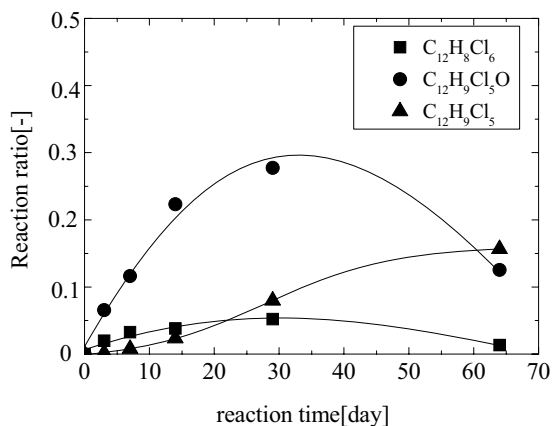


Fig. 3. Generation of reaction intermediate by ferric iron (1) and by ferric iron + reduced copper (2) with time. The intermediate molecules are normalized initial dieldrin molecular number.

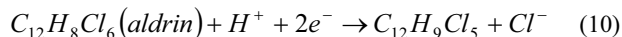
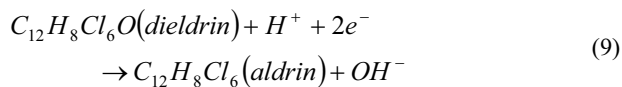
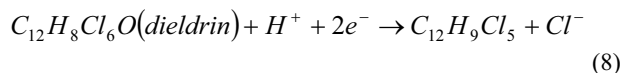
TABLE II
 PSEUDO-FIRST-ORDER INITIAL RATE CONSTANTS OF DDEGRADATION OF
 DIELDRIN BY FERRIC SULFIDE IN THE CLOSED SYSTEM FOR DIFFERENT OXYGEN
 VALUES

O ₂ [μmol]	0	10	50	100	300	Air
k	0.105	0.145	0.123	0.078	0.046	0.023

k: pseudo-first-order reaction rate constant of equation (1)

B. Degradation Process in Ferric Iron

In the case of metallic iron powder, dieldrin underwent partial dechlorination to yield only its mono-dechlorination products (C₁₂H₉Cl₅, C₁₂H₉Cl₅O) and aldrin (C₁₂H₈Cl₅). Reaction products are shown in Figure 3. No aqueous products were detected in ferric iron with/ without reductant. This reaction proceeded by reductive hydrodechlorination with the generation of H⁺, which generated by oxidation of ferric iron. The following chemical reactions (8)-(10) are assumed as dechlorination of dieldrin.



Dieldrin was mainly degraded to aldrin which continuously degraded to mono-dechlorinated intermediate. This reductive reaction was accelerated by reductant but mono-dechlorination intermediates were also accumulated. In the case with ferric iron, it has a high dechlorination ability of dieldrin, but entire detoxination could not prospect in remediation.

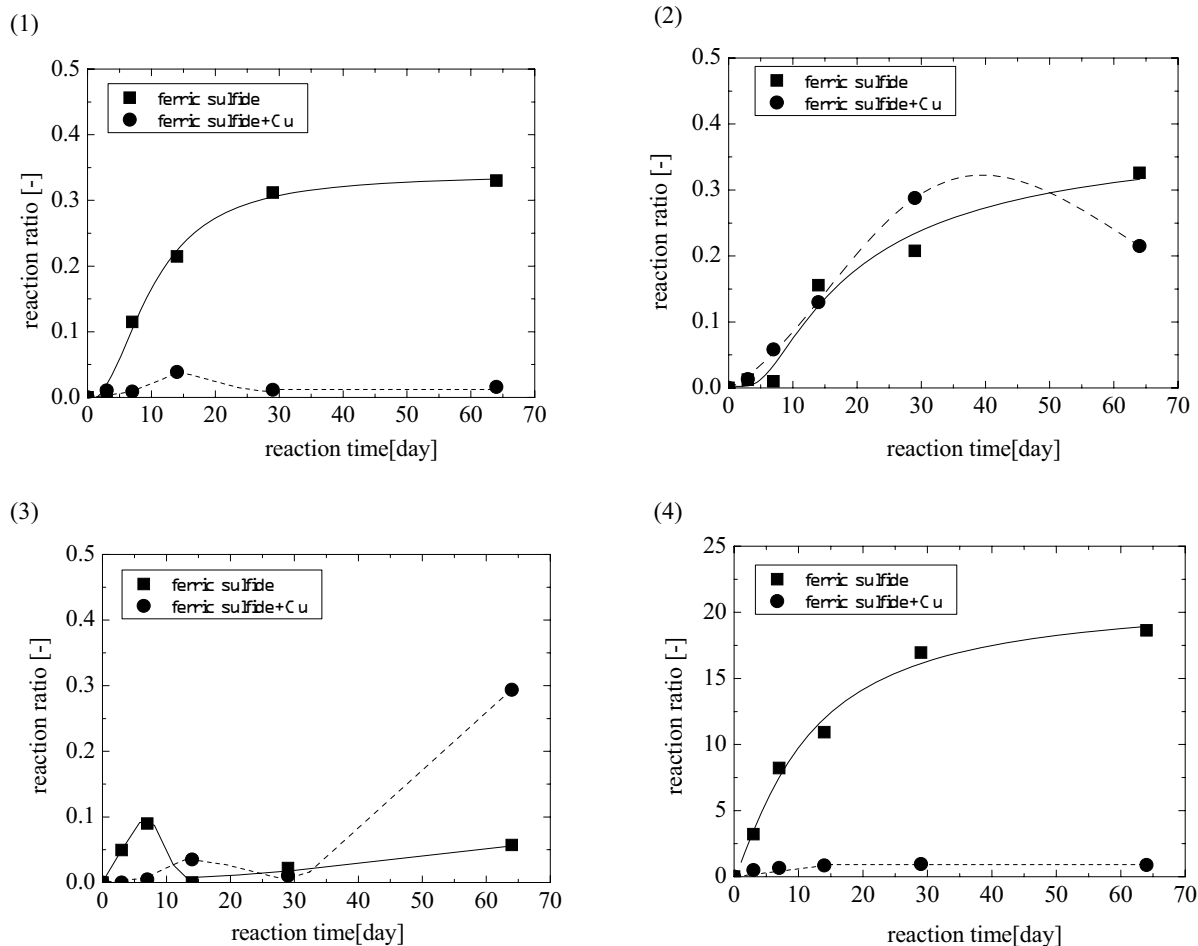
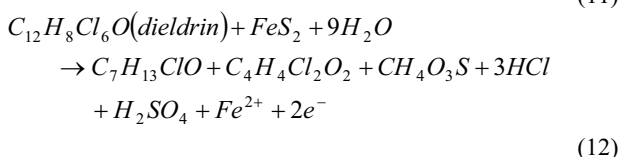
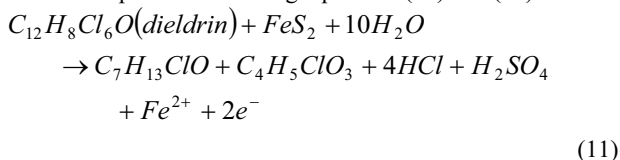


Fig. 4. Generation of reaction intermediate by ferric sulfide and by ferric iron + reduced copper with time. The intermediate molecules are normalized initial dieldrin molecular number. (1) heptanoyl (C₇H₁₃ClO), (2) Cl⁻ + ethyl chloroglyoxylate (C₄H₅ClO₃), (3) succinyl chloride (C₄H₄Cl₂O₂) (4) SO₄²⁻ + methanesulfonic acid (CH₄O₃S). Sulfuric acid and methanesulfonic acid were generate with concerned with dissolution of ferric sulfide.

In the previous remediation research using metallic catalysis also shows the same results as this result [8]. The selective reduction of a chlorine at the bridgehead carbon in the reaction of dieldrin over metallic catalysis is intriguing, since the proton is usually the most difficult to reduce. If hydrogen injected in the metallic catalysis system with dieldrin, chlorines at bridgehead carbons never reduced. The reductive degradation by metallic catalysis is available for entire remediation of chlorinated ethylene or ethane, but this reducing activity is inadequate to dechlorinate dieldrin entirely.

C. Degradation process in ferric sulfide

Different from reductive dechlorination by ferric iron powder, oxidative degradation was observed in the reaction with ferric sulfide, and the stable chemical structure of dieldrin was decomposed into water-soluble intermediates, heptanoyl ($C_7H_{13}ClO$), ethyl chloroglyoxylate ($C_4H_5ClO_3$), methoxyethane (C_3H_8O), succinyl chloride ($C_4H_4Cl_2O_2$) and methanesulfonic acid (CH_4O_3S). Time profile of reaction intermediate was shown in Figure 4. These reaction intermediates have no chemical structure of drin class. The mono-dechlorination products which generated in the case of reaction with ferric iron were not detected. Ferric sulfide has strong degradation ability. These oxidative dechlorinations are assumed to proceed following equations (11) and (12).



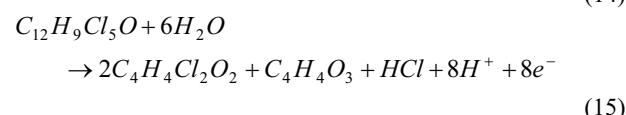
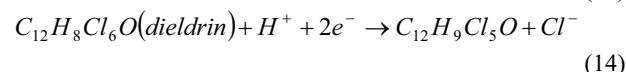
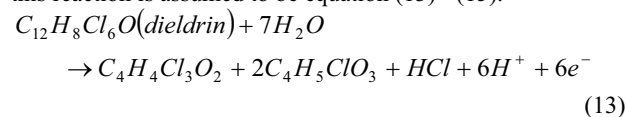
The catalytic dechlorination by ferric sulfide (especially pyrite) intended for several chlorinated ethylenes or carbon tetrachloride shows entire dechlorination of chlorinated chemicals [15], [20]-[23]. Concerning with the dechlorination of chlorinated thylenes, some report shows the reductive dechlorination under anaerobic condition, in which chlorinated ethylenes transform to ethylene or ethane as final products, and some report shows the oxidative dechlorination under aerobic condition, in which CO_2 was detected as final products. On the other hand, oxidative reaction is also reported for dechlorination for carbon tetrachloride under anaerobic and aerobic conditions. In this way, dechlorination mechanism by ferric iron (pyrite) is expected to be sensitive for the co-existing minor metallic element or surface condition of pyrite.

Borda (2003) intimately reported the oxidation mechanism of pyrite [24]. The surface of pyrite is capable of dissociating H_2O to form OH^\bullet (hydroxyl radical), then a fraction of OH^\bullet combines to form H_2O_2 in solution and a fraction of OH^\bullet reacts to oxidize sulfur at the pyrite surface. This initial reactivity appears to precede further pyrite oxidation by other oxidants, such as O_2 .

The hydroxyl radical and hydrogen peroxide have a high potential of dechlorination for chlorinated organic compound, as Fenton reaction. Additionally, chlorinated organic compounds are easily oxidizable by pyrite than water. In our

experiments, dieldrin transformed to reaction intermediate by oxidative dechlorination in ferric sulfide system. This dehalogenation assumes to occur via the adsorbed hydroxyl radical generated on the surface of ferric sulfide. The surface character of pyrite is a hydrophobic one and it also assists the adsorption of dieldrin on pyrite.

In addition, the initial rate of oxidative dechlorination by ferric sulfide was retard by the addition of reductant. As show in Figure 1, simple deduced copper have not an activity of the dechlorination of dieldrin, but it facilitated the reductive dechlorination in ferric iron system, and retarded the initial oxidative reaction in ferric sulfide system. The retardation of initial oxidation was assumed that equation (11), (12) did not proceed by the existence of reductant, because the production of SO_4^{2-} , methanesulfonic acid and heptanoyl was decreased by the addition of reduced copper. Main reaction intermediate in the initial oxidation were ethyl chloroglyoxylate and succinyl chloride. In initial reaction process, succinyl chloride was assumed to be dechlorinated to succinic anhydride by hydrolysis [25]. Following to initial oxidative dechlorination, mono-dechlorinated intermediate also detected as the reaction in ferric iron system (Figure 5). Although first oxidative degradation hardly proceeded, ferric ion which generated by the dissolution of ferric sulfide induce reactive degradation and generate mono-dechlorination intermediate ($C_{12}H_9Cl_5O$). This intermediate was also degraded to succinyl chloride by oxidative reaction. This complex reaction was observed though reductant added ferric sulfide system. The stoichiometry for this reaction is assumed to be equation (13) - (15).



As mentioned above, the final succinyl chloride is easily hydrolyzed to succinic anhydride and decomposed in environment. The entire dechlorination is expected by the addition of reduced copper in ferric sulfide system. The final

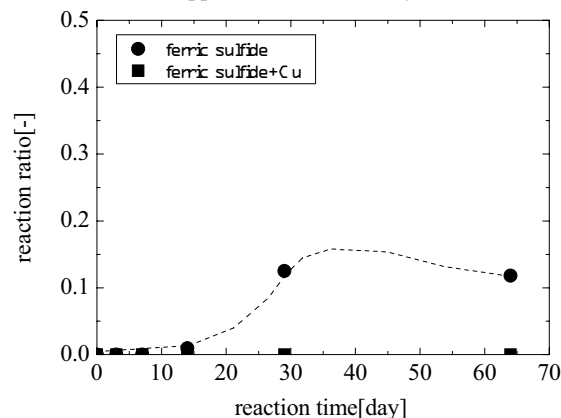


Fig. 5. Generation of $C_{12}H_9Cl_5O$ by ferric sulfide and by ferric iron + reduced copper with time. The molecules are normalized initial dieldrin molecular number.

pH in this system does not bring acidification of soils. This is also a proper treatment in environments.

IV. CONCLUSION

The dechlorination mechanism of dieldrin was different from the species of metallic catalysis. In the ferric iron system, dieldrin transformed to mono- or di- dechlorinated intermediates by reductive dechlorination. The chemical structure of dieldrin could not be decomposed. On the other hand, dieldrin decomposed to low molecular aqueous organic intermediates in ferric sulfide system by oxidative dechlorination. The entire dechlorination will also be expected by the addition of reduced copper in ferric sulfide system.

The previous studies using bioremediation techniques or metallic catalysts reported that complete dehalogenation of dieldrin under anaerobic conditions is difficult, as found in our metallic iron experiments. Our research suggests that ferric sulfide is capable of strong degradation for dieldrin and complete degradation was expected under ferric sulfide and reduced copper mixing system. However, the laboratory kinetic and reaction process of dieldrin transformation by ferric sulfide are not yet extrapolated to field condition. The effects of natural organic matter, chemical composition of soil matrix, competing oxidants, co-solvents and different environmental conditions can confound the reactivity, and they need to be made obvious by qualitatively comparing. Further research is expected to bring a useful in-situ remediation technique.

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