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Thermal Remediation of Dioxins Contaminated Soil and Fry Ash by Zone Combustion Process(ゾーン燃料プロセスによるダイオキシン類汚染土壌および飛灰の浄化)

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論文内容要旨

Chapter 1 [Introduction]: Major sources and inventory of the polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) or dioxins emission were described. The state of arts of the science and terminology relating to the dioxins, its formation in the thermal processes and the suppression of their emission was introduced. It is appeared that PCDD/Fs contamination and accumulation into soil through atmospheric deposition and other possible sources are so persistent. Therefore, it is urgently required to develop an effective remediation technology to clean up the soil with high efficiency.

Chapter 2 [Review of PCDD/Fs Remediation Technologies]: Previous remediation technologies of PCDD/Fs were reviewed. It shows that they can be sorted into several categories such as bioremediation, physical/chemical and thermal remediation. It is pointed out that the thermal remediation is the most reliable process at present, in terms of the removal/decomposition efficiency of dioxins, the capacity of handling mass and probably the cost.

Chapter 3 [Zone Combustion Process]: A new concept of the thermal remediation technology, namely zone combustion process, of particulate/powder materials contaminated by dioxins are proposed. The process is based on the packed bed combustion of carbonaceous fuel like coke mixed with particles/powders. It is basically a one-dimensional unsteady-state process; however, it can be extended to a two-dimensional steady-state process. The latter can be a continuous process, which is suitable to remedy a large amount of solid materials. **Fig. 1** and **Fig 2** show the continuos practical image of two-dimensional steady state and its concept in one-dimensional unsteady state, respectively.

Chapter 4 [Process verification]: Some basic and fundamental studies on zone combustion process were divided into several chapters in the thesis. In this chapter, the validation of the zone combustion process in the remediation of dioxin-contaminated soil was discussed. The apparatus is based on one-dimensional unsteady-state process (see **Fig. 3**). It consists of a cylindrical reaction pot, which is made of stainless steel and can be opened vertically into two parts. The inside diameter and height of the pot is 110 and 300 mm, respectively. Alumina fiber sheet was used as lining of the inside surface of the pot for insulation. At the bottom of the pot, a stainless steel mesh plate and a thin bed packed with alumina ball of 6 mm in diameter were put as substrates. Temperatures of the bed were measured with a lapse of time by thermocouples inserted

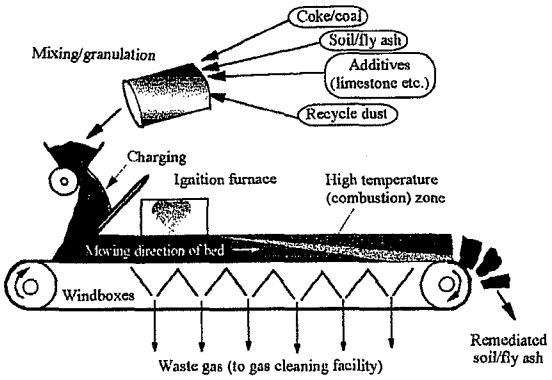

Fig. 1. Practical image of a continuos zone combustion process.

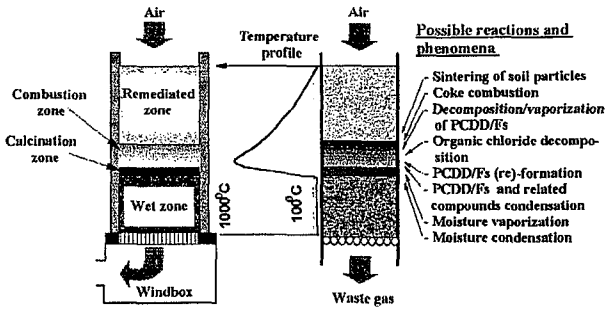

Fig. 2. Possible reactions and phenomena in the zone combustion process.

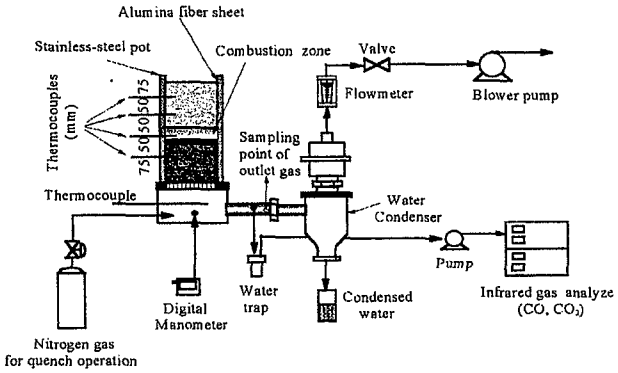

Fig. 3. Experimental apparatus.

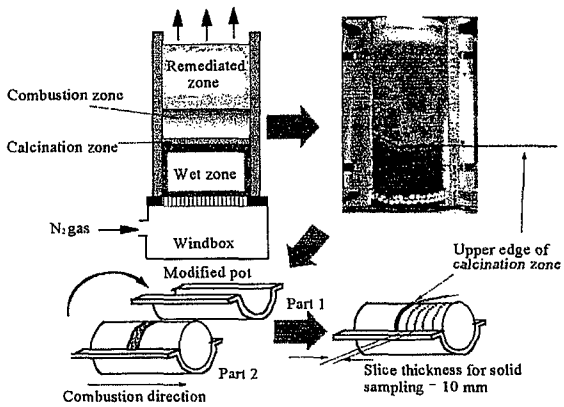

Fig. 4. Sampling of the quenched bed.

at 75, 125, 175 and 225 mm from the top of the bed. In this study, only combustion experiment was conducted to get solid samples of the remediated soils. Only, tetra- to octa-homologues of the solid and gas samples were analyzed for all studies.

PCDD/Fs contaminated soil from a site near industrial waste incinerators was sampled. The level of PCDD/Fs was 13 ng/g-dry or 330 pg-TEQ/g-dry. The mixtures prepared under different pretreatment conditions were subjected to the combustion zone experiment. The results show that the removal ratio of dioxins reaches more than 99% (same in TEQ). When the soil is pre-treated by the drying or limestone addition, the removal ratio increases up to 99.9% (99.99% in TEQ). The capacity of the process was evaluated very large, about 0.4 Mg-dry/m^2/h, that is, 3,500 ton-dry/m^2/year.

Chapter 5 [The presence of organic chloride]: It deals with the formation of dioxins during the process when soil to be remedied contains organic chlorides. The sample mixture was prepared from soil, coke and PVC polymer powder. The relatively 'clean' soil (PCDD/Fs: 263 pg/g-dry or 2.0 pg-TEQ/g) was used in order to provide a clear observation of the PCDD/Fs formation, which may occur during the thermal process due to the presence of organic chloride. Coke was sized between 1 and 3 mm, and its mixing ratio was set at 7.5 mass%. The average molecular mass and particle size of the PVC polymer were 1100 and 0.33 mm, respectively. The mixing ratio of PVC to soil was 1000 ppm on the chlorine basis. The distribution of PCDD/Fs concentration, as well as moisture, chlorine and alkaline earth, of the quenched bed in the vertical direction was obtained by introducing reverse flow of nitrogen rapidly from the bottom of the bed during

experiment (see **Fig. 4**). Dioxin concentration in the exhaust gas was also analyzed according to Japanese Industrial Standard (JIS) K 0311.

It was confirmed that the process could efficiently remove dioxins originally contained in the soil. However, chlorides contained in the soil can be a chlorine source of a new formation of dioxins during the process. The results show that dioxins formed in the bed were transferred downward with gas stream through the bed and trapped at the lower bed (see **Fig. 5**). In such a way dioxins move through the bed and exhausted with the outlet gas. Chlorine also moves down through the bed as the process progresses. Alkaline and alkaline earth compounds play important roles in the transport phenomena of chlorine.

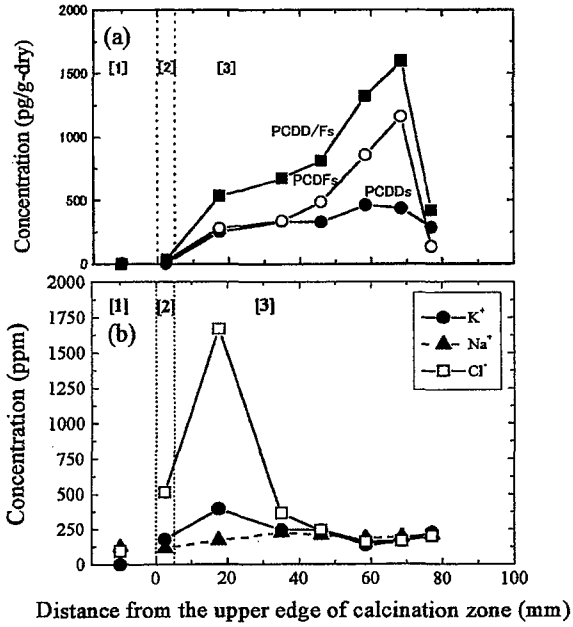

Fig. 5. Distribution concentration of PCDD/Fs (a) and some elements (b), in the quenched bed. ([1] remediated, [2] calcination, and [3] wet zones)

Chapter 6 [Dioxin Behavior]: Behavior of dioxins in terms of transport and fate during the process was experimentally examined by employing octachloro-dibenzo dioxin spiked with ^{13}C (^{13}C-OCDD) as a homologue model.

The process removes dioxins from the solid materials through their decomposition and vaporization. However, there is also a possibility of new formation of dioxins during the process. The soil contains ^{13}C-labeled OCDD was used to distinguish the originally contained dioxins from the newly formed ones. The concentration of ^{13}C- OCDD in the feed mixture was 1600 pg/g-dry with the coke content was set at 7.5 mass%-dry. The result shows that the decomposition ratio of the originally added ^{13}C-OCDD is as large as about 98.6% (see **Fig.6**). This appears to occur mainly through an oxidative thermal degradation rather than dechlorination since any other ^{13}C-labelled homologues were detected in the neither remedied soil nor the exhaust gas. It was also observed that the transformation of ^{13}C-OCDD occurred through the bed.

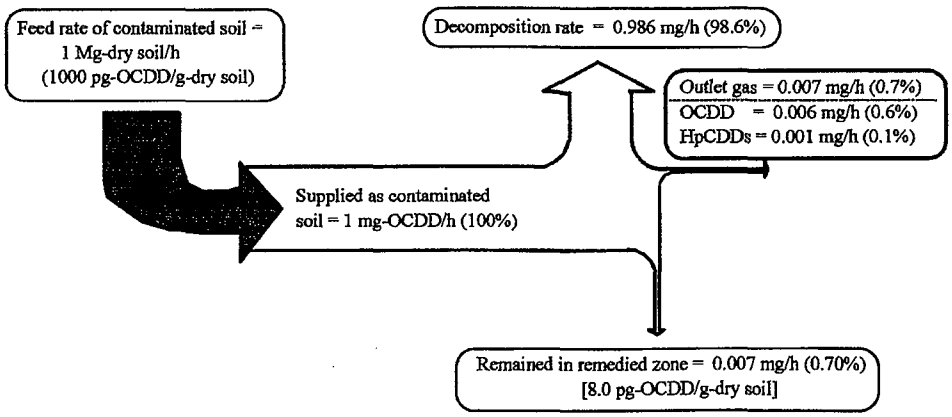

Fig. 6. Mass balance of ^{13}C-OCDD in the zone combustion process.

Chapter 7 [Application to fly ash]: An attempt to remedy dioxin contaminated in fly ash of municipal solid waste incinerator (MSWI), which usually contains high concentration of original chloride compounds, was undertaken. In the base experiment, fly ash and 11 mass%-dry coke were simply mixed and granulated with the addition of the sprayed water. For the comparison, another experiment was conducted with the addition of 2 mass%-dry urea, to examine the effect of an inhibitor on the PCDD/Fs formation during the process. Fly ash contains a large amount of chlorine (13.4 mass%), volatile matter (7.1 mass%), unburned carbon (2.1 mass%) and many metallic compounds.

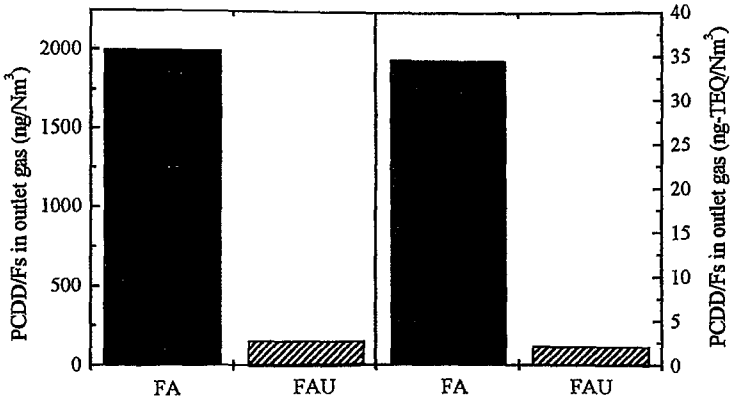

Fig. 7. PCDD/Fs concentration in the outlet gas

The remediation using the fly ash without any pretreatment except for addition of coke as fuel gives fairly high removal efficiency of dioxins. However, the concentration of dioxins in the exhaust gas was considerably high. It may be because the sufficient chlorine source and metallic catalysts exist in the fly ash. On the other hand, the addition of urea (2 mass%-dry) can reduce the concentration of PCDD/Fs in the outlet gas by about 92.7% (see **Fig.7**). Although further study is necessary, the effect of the urea seems to be attributed to the reduction of chlorine potential through the formation of NH_4Cl and further poisoning of the catalytic compounds for the dioxin formation in the bed.

Chapter 8 [Conclusions]: The zone combustion process is proposed as a new thermal remediation technology of dioxins contaminated soil and fly ash with the characteristics of high handling mass capacity and relatively low cost. It was verified that the removal efficiency of the process to remedy PCDD/Fs contaminated soil was more than 99% with the capacity reaches 3500 ton-dry/m^2/year. The presence of organic chlorides in the soil leads to the new formation of PCDD/Fs during the process. The newly formed PCDD/Fs in the bed are transferred downward with the gas stream through the bed and trapped at lower bed. In such a way, PCDD/Fs moves through the bed and is exhausted with the outlet gas. Chlorine moves down through the bed as the process progresses. Alkaline and alkaline earth compounds play important roles in transport phenomena of the chlorine. The ^{13}C-OCDD was added to the soil to distinguish the originally contained PCDD/Fs from the newly formed. The result shows that the decomposition ratio of the originally added ^{13}C-OCDD is as large as 98.6%. This appears to occur mainly through an oxidative thermal degradation rather than dechlorination. In the application of the process to the fly ash without any pretreatment, except coke for fuel, gives fairly high removal efficiency of PCDD/Fs. However, the concentration of PCDD/Fs in the exhaust gas was considerably high, probably due to the existence of chlorine source and metallic catalyst in the fly ash. By adding urea as an inhibitor (2mass%-dry) in the feed, the emission of PCDD/Fs is suppressed by about 92.7%.

論文審査結果の要旨

2000年に施行されたダイオキシン類対策特別措置法などの効果により、我が国における環境へのダイオキシン類排出量は大幅に減少している。しかし、従来の排出等による土壌汚染等が指摘され、効率的な浄化法の開発が望まれている。本研究は、粉粒状汚染物質の高効率浄化が可能な新しい技術原理を提案し、実験的に検証したものである。本論文はこれをまとめたものであり、全7章より構成される。

第1章は緒論であり、ダイオキシン類の性質、廃棄物焼却炉などの高温プロセスからの排出、環境中挙動について概説し、生成メカニズムに関する従来の所見を記述している。さらに、本研究の目的と本論文の各章を概説している。

第2章では、ダイオキシン類および関連化合物に汚染された土壌と飛灰の浄化技術に関する従来の研究開発動向を総括した。汚染土壌や飛灰の処理技術をその技術原理より、1) 生物処理、2) 物理的・化学的処理、3) 高温処理の3つに分類し、各分類における代表的なプロセスを概説すると共に、それぞれの利点および問題点を整理している。

第3章では、本研究で提案するダイオキシン類汚染土壌の新しい浄化プロセス「ゾーン燃焼プロセス」について、その概念と特徴を述べている。これは、炭材粒子を汚染土壌と混合・造粒し、充填層を形成させた後、層頂から順次燃焼させる、充填層炭材燃焼プロセスである。本プロセスの利点を予測する一方、層内での新たなダイオキシン類生成の問題を指摘し、本研究の具体的な課題を整理している。

第4章では、ダイオキシン類を含む土壌を試料とする浄化実験を行った結果を記述している。土壌試料は産業廃棄物焼却炉が近接する場所から採取した。単純にコークスを混合した試料においても99%の毒性除去率が得られ、予備処理の併用により、99.99%の毒性除去率を達成するなど、本プロセスの妥当性を検証した。

第5章では、被浄化土壌中に塩素化合物、特に有機塩素化合物が含まれる場合について、新たなダイオキシン類の生成とその挙動について検討した。反応中断実験により層内のダイオキシン類の挙動を詳細に調査した。土壌試料が塩素化合物を含有しても浄化後の土壌には残留せず、排ガス処理は従来技術で対応可能と考察した。

第6章では、被浄化土壌中に含まれるダイオキシン類の浄化処理中の挙動を定量的に把握するため、^{13}C 同位体によりラベル化したOCDDを予め土壌試料に混合した、モデル実験を行った。土壌中に含まれるOCDDの98.6%は本プロセスにより分解され、脱塩素化等による他の異性体生成も検出限界以下であることを確認した。

第7章では、本プロセスを廃棄物焼却飛灰へ適用するための実験的な検討を行った。排ガス中のダイオキシン類含有量の増加を抑制するために、ダイオキシン類生成抑制剤としての効果が報告されている尿素を混合した浄化実験を行い、排ガス中ダイオキシン類が約1/10に低減できることを確認した。

第8章は、結論であり、上記各章を総括している。

以上、要するに本論文は、ダイオキシン類に汚染された土壌や飛灰を効率的に浄化可能な新しい技術原理を提案し、実験的に検証したものであり、環境からの有害有機化学物質の除去技術の高度化と廃棄物処理工学および環境工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。