

A NEW REMEDIATION TECHNIQUE FOR SOILS CONTAMINATED WITH DIOXINS EMPLOYING VACUUM PYRORISIS

Tsuyoshi Abe, Hitoshi Mizuno, and Kenji Noguchi

Research and Development Division, Houei Shokai Co. Ltd, Teraike 66, Tsutsumi-cho, Toyota, 473-0962, Japan

Introduction

Many remediation techniques for dioxins from contaminated soils and fly ash have been developed. However, since we have the successful technology of recovering zinc from zinc-plated steel by vacuum heating, we have applied this technique to decontaminate the contaminated soils and ash. Two highly contaminated soil samples with PCDDs, PCDFs, and Co-PCBs were heated at 800, 1000, and 1200°C for four hours in a vacuum chamber at pressures from 0.5 to 50 Pa. Concentrations of dioxins in the processed residues are found to be close to or lower than the detection limits. The amounts of dioxins evaporated from the soil samples were observed at the various points of the pumping line and we find that their concentration levels are also much lower than the regulation levels. Furthermore, at these temperatures heavy toxic elements, such as Zn, Cd, and Pb, are found to evaporate from the soil samples and trapped as metals in the condenser cassette. Therefore, using the present technique, not only dioxins but also heavy metals can be removed from the soil.

This study aims at developing a high cost-performance remediation technique which may be applicable for cleaning the contaminated soil in large quantities without extracting dioxins and thus may cost less. Further, since materials evaporate at lower temperatures under vacuum than their boiling points, this technique is expected to become an energy-saving one. As far as the authors know, no studies have been made on the vacuum heating treatment of the contaminated soils with dioxins at such high temperatures.

Methods and Materials

For this study, we constructed new equipment which is capable of heating samples in vacuum up to 1200°C. It consists of a main chamber for loading a sample is connected to a pumping system with a mechanical booster pump backed by a rotary pump as well as a gas cracker chamber (which can be heated up to about 1200°C), an oil mist trapper and a condenser which are installed between the main chamber and the pumping system. A scrubbing unit is connected after the rotary pump. The gaseous fractions evaporated from the heated sample pass through the gas cracking chamber but organic compounds formed from the soil samples are pyrolyzed to smaller molecules. To make the residence time within the gas cracker, alumina (Al₂O₃) balls are filled in it. The condenser is a cassette for accumulating metals evaporated from the samples. The scrubbing unit washes out acidic gases by alkali showers, the pH of which is monitored and controlled in the range from 10 to 12. After the scrubbing unit, a charcoal filter is connected for absorbing dioxins, if any.

In order to prevent dioxins from entering the pumping system, after the sample is loaded, the gas cracker is heated to about 1200°C, before heating of the sample is started. As the temperature of the sample chamber is raised, the pressure increases since the gaseous decomposition products are formed from the heated soil as well as in the gas cracking-chamber. The pressure in the chamber

ORGANOHALOGEN COMPOUNDS

Vol. 54 (2001)

varies with the sample temperature. The heating rate is regulated so that the pressure ranges from 1 to 200 Pa. After four hours of heating at the preset temperature (800, 1000, and 1200°C), the sample chamber is cooled under vacuum.

Two soil samples used for this study are contaminated with dioxins (PCDDs, PCDFs and Co-PCBs) and heavy metals such as lead. Soil A contains 6300 pg-TEQ/g and soil B 5500 pg-TEQ/g of dioxins. These soil samples were processed at 800 and 1000°C.

Results and Discussion

The concentrations of PCDDs, PCDFs, and Co-PCBs in untreated soil A and B are summarized in Table 1. Tables 2 and 3 summarize the concentrations of dioxins in the residues of the soils processed at 800 and 1000°C, respectively. One can obviously see from Tables 2 and 3 that essentially no dioxins remain in the treated residues.

Table 1. Amounts of PCDDs, PCDFs, and Co-PCBs in untreated soil A and B.

		PCDDs	PCDFs	Co-PCBs	Total Dioxins
Soil A	pg-TEQ/g	2000	4300	40	6300
	pg/g	220000	240000	9700	470000
Soil B	pg-TEQ/g	1000	4500	22	5500
	pg/g	110000	270000	2100	380000

Table 2. Concentrations of dioxins in the residues of the soils processed at 800°C

		PCDDs	PCDFs	Co-PCBs	Total Dioxins
Soil A	pg-TEQ/g	0	0.00072	0.00059	0.0013
	pg/g	0.21	0.96	3.6	4.7
Soil B	pg-TEQ/g	0	0	0.000082	0.000082
	pg/g	0.065	0.18	0.88	1.1

Table 3. Concentrations of dioxins in the residue of the soils processed at 1000°C

		PCDDs	PCDFs	Co-PCBs	Total Dioxins
Soil A	pg-TEQ/g	0	0.0044	0.00019	0.0046
	pg/g	2.9	2.3	2.5	7.7
Soil B	pg-TEQ/g	0	0	0.00014	0.00014
	pg/g	1.9	1.3	1.9	5.0

Concentrations of PCDDs, PCDFs, and Co-PCBs were analyzed in the oil mist trapper (oil), rotary pump oil, scrubbing unit (alkali sol.), and charcoal filter as well as exhaust gases from the filter and the results are listed in Table 4. Exhaust gas (a) and (b) were collected before and after attaining the processing temperature, respectively. Neither the residual soil samples nor the exhaust gas contains the regulated levels of dioxin concentrations in Japan. Hagenmaier et al. have shown that heating the fly ash from a municipal incinerator at 300°C the dioxins' concentrations considerably decrease in pure N₂ atmosphere but dramatically increase in a flowing air¹. In the present experiment conditions are similar in the sense that

Table 4. Dioxins concentrations observed at various points of the vacuum system.

		Soil A	Soil B
Oil mist trapper	ng-TEQ/g	0.00030	0.0063
Rotary pump oil	ng-TEQ/g	0.00053	0.00055
Scrubbing unit	pg-TEQ/l	0.044	0.00051
Charcoal filter	ng-TEQ/g	0.00000014	0.00000015
Exhaust gases (a)	ng-TEQ/m ³ N	0.0000011	0.0000050
Exhaust gases (b)	ng-TEQ/m ³ N	0.0000020	0.0000053

no oxygen gas is present. The strongly reducing conditions of fly ash surfaces may have prevented the oxidation and chlorination reactions of the low chlorinated dioxins from forming heavily chlorinated dioxins and re-synthesizing heavily polychlorinated dioxins from organic precursors on fly ash surfaces. Further under vacuum, any precursor molecules with low molecular weights are pumped away and this makes the treated fly ash "cleaner." These features distinguish this method from the pyrolysis method in an ambient atmosphere

The residues are mostly inorganic and major minerals preserve their original structure. From the SEM-EDS study, wurtzite is reduced to magnetite, and one observes a zoning structure on the K-feldspar grains resulting from reduction. The results show the surface conditions of fly ash are highly reductive. It is thus reasonable to consider that the low pressure and reductive surface conditions suppress formation of PCDD/Fs.

Acknowledgements

The authors greatly acknowledge helpful discussions with Prof. K. Shobatake of Nagoya University. The authors thank Drs. Yasuji Saito and Kazumi Yokoyama of National Science Museum for supporting mineralogical analysis and arguments. This research was only possible with the generous support of Mr. Toru Kodama, the president of Hoei-shokai Co., Ltd.

References

1. Hagenmaier H., Kraft M., Brunner H., and Haag R. (1987) Environ. Sci. Technol. **21**, 1080.