MECHANICAL ACTIVATION OF PCDD/PCDF-CONTAINING MATERIAL

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Introduction

In case of the pyro-metallurgical recycling of copper from cable scrap, dust with high concentrations of polychlorinated dibenzodioxins and –furans (PCDD/F) comes up. Especially high pollution can be found at old factories which need an expensive rehabilitation when they are shut-down. This can mean that a big part of the building material (masonry, concrete) of the respective factory has to be disposed of in underground mines. It was the aim of this examination to check whether in case of intensive grinding of polluted fabric of a building, mechano-chemical reactions can be triggered off which entail a destruction of PCDD/F.

Methods and Materials

The initial material was a highly concentrated dust of a shut-down copper smelter with a PCDD/F concentration of 22,8 µg I-TEQ/kg dry weight. This dust was mixed with 75 % concrete of grain size 100 % < 100 µm in order to simulate polluted fabric of a building. On the one hand a ball mill and on the other hand a vibratory mill were used for grinding. While ball mills fundamentally exert a grating stress, the main stress in case of vibratory mills is impact. In case of this impact, the crystal lattice is disordered additional to enlargement of the surface which leads to an increase of the enthalpy of the crystalline system and which triggers reactions of solids in the presence of suitable reaction partners. This effect is set off when grinding dioxin-containing dusts together with concrete or masonry in a vibrating mill. It is assumed that the Cl groups of PCDD/F together with calcium form stable calcium chlorides which excludes a back-formation of PCDD/Fs after the grinding. The effect of the mechano-chemical reaction during grinding processes known in the metallurgy was applied to the conversion of dioxins and furans by means of different additives.[1] In the present work we investigated the use of building fabrics in mechano-chemical PCDD/F conversion which has not yet been considered in previous works.
The material, referred to in the following as "input" as well as the treated samples were subjected to a treatment with HCl before the examination on PCDD/F.[2] After 16 hours of extraction in a soxhlet with toluene/acetone (90/10) the samples were cleaned up by means of silicagel and alumina in a process of several stages. The analysis was done by means of HRGC/HRMS with a HP5890A/VG AutoSpec system.

Results and Discussion

In Figure I the changes of the I-TEQ value at an increasing period of grinding of the described mixture in the ball mill and vibratory mill are compared. Even after an extremely long grinding period of 10 hours, no significant reduction in PCDD/F concentration can be observed in case of the ball-mill grinding. With regard to the vibratory mill, however, an 80 % decrease of the I-TEQ value has already been reached after 3 hours. This impressively proves the decisive influence of the impact-exerted stress.

Figure 2 and 3 reflect the stronger breakdown of higher chlorinated congeners.

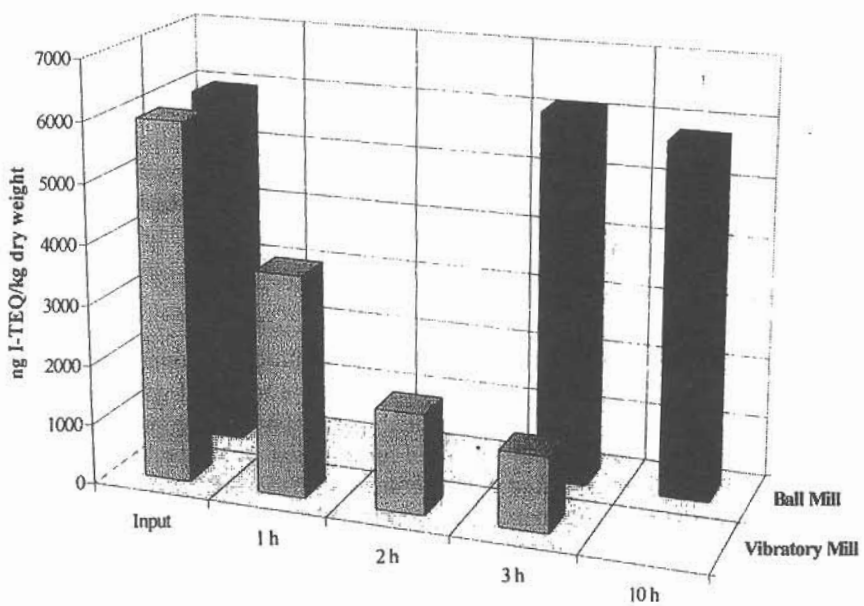


Figure 1: I-TEQ value after the grinding of mixtures of highly PCDD/PCDF-polluted dusts from the recycling of copper in a ball mill or a vibratory mill.

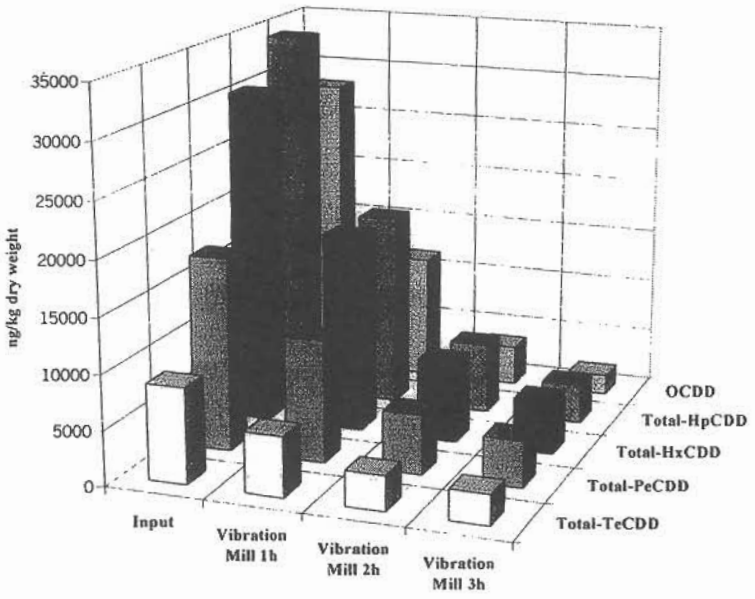


Figure 2: Decrease of concentration of PCDD depending on the period of grinding in a vibratory mill.

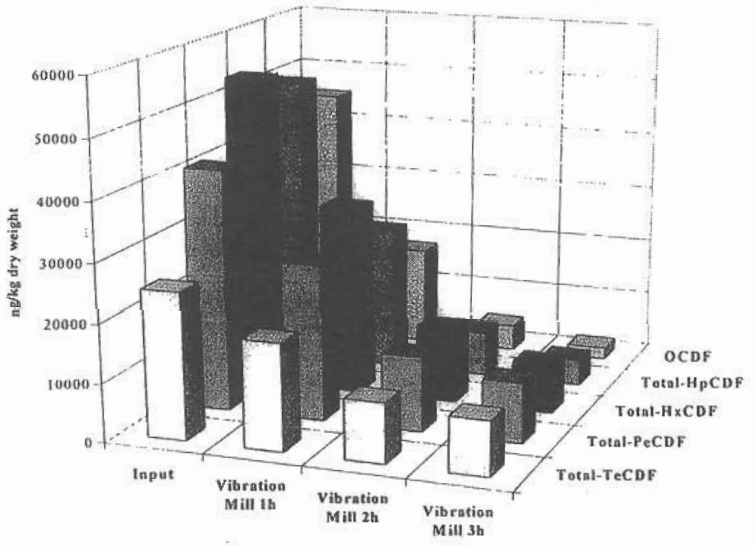
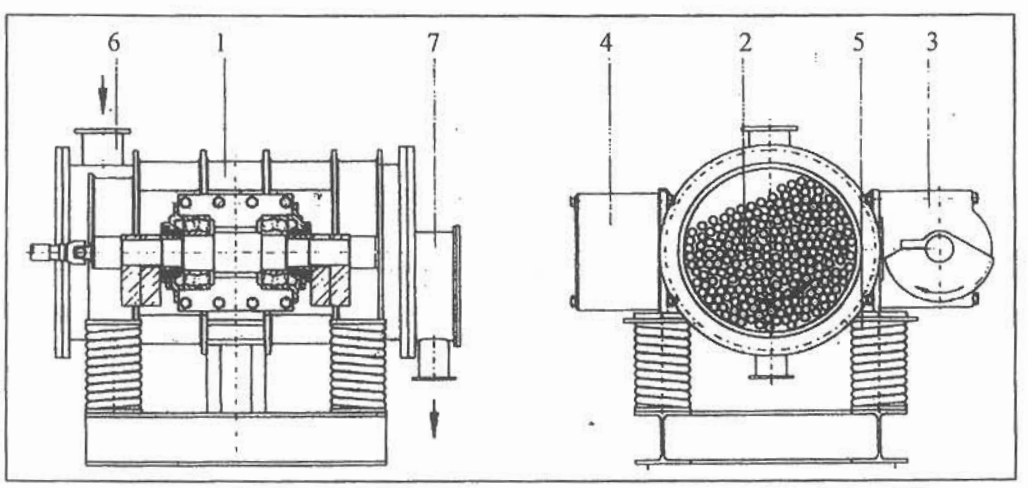


Figure 3: Decrease of concentration of PCDF depending on the period of grinding in a vibratrory mill.

Compared with high-temperature processes the use of grinding machines in order to destroy PCDD/F is a simple technology which can also be used efficiently for small quantities. As described, the way in which power is exerted plays an important role. As the impact-exerted stress is of decisive importance in order to trigger mechano-chemical reactions only vibratory mills can be considered.
During the last 5 years there have been crucial further developments on this sector. A single-tube vibratory mill, the "Eccentric Vibratory Mill" (ESM) which stands out compared to the conventional vibratory mills thanks to the reduction of the specific energy requirement by 50 % has been developed. The module-like construction (vide Figure 4) makes it possible to adjust the machine to any degree of reduction by variation of the tube length.



1 grinding chamber 2 grinding medium 3 excitation unit
4 balancing weight 5 screw spring 6 socket for filling
7 discharge

Figure 4: Construction of a module of the Eccentric Vibratory Mill (ESM)[3, 4]

Acknowledgements
We gratefully acknowledge the help of Thomas Ohlmann in performing part of the experiments.

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ORGANOHALOGEN COMPOUNDS

Vol. 54, 2001