Dioxin separation with natural zeolites

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Introduction

Reported on in the following is the separation of dioxins and furanes to a mineral adsorbent.

The separation of dioxins and furanes (PCDD/F) from thermal (incineration)processes is an essential component in the job of keeping the air clean. The limit value applicable for waste incineration plants, in accordance with the 17th ordinance regarding enforcement of the Federal Emissions Protection Law (17^{th} BImSchV), is 0.1 ngTE/m^3 for PCDD/F as related to standard conditions, dry and an 11 % oxygen content. In other branches of industry, like for instance secondary raw materials recycling in metallurgical processes, the responsible authorities demand that an emission concentration of 0.1 ngTE/m^3 be observed.

The implementation of activated carbon has proven its worth in gas purification, particularly through the great multitude of separable pollutants. For dioxins and furanes, separation results of over 99 % are achieved at present, depending on the peripheral operating conditions at hand. That would be, apart from the input, i. e. feedgas concentration, the adsorbent implementation, either as pure product in a moving bed or an entrainment process or as mixed adsorbent with a corresponding inert material for PCDD/F separation, generally a calcium compound.

As activated carbon is generally combustible due to its high carbon content, the demands to be observed with respect to safety engineering are accordingly high, namely, preventive measures for fire and explosion protection must be taken. This entails additional investment operational costs.

Other non-combustible adsorbents that also exhibit a highly selective separation behavior due to their inner structure are the zeolites. Gas purification with zeolites has been known for quite some time and is implemented in the most diverse of processes. Zeolites are found in nature or are produced synthetically. Because synthetic zeolites are very expensive to produce, their utilization in flue gas purification is, for reasons of cost, generally not done. The implementation of natural zeolites for flue gas purification therefore represents an approach towards a cost-optimized operation of such plants, as such zeolites are considerably less expensive than those which are synthetically produced.

Zeolites, i. e. zeolithic mineral rocks, consist mainly of silicates and have, because of that, the natural advantage of non-combustibility which is equally advantageous for both handling and operation.

In Bötzingen-am-Kaiserstuhl a volcanic rock called phonolite is strip mined. This material has a zeolite content of 45 %. The mineralogical and chemical data for phonolite are given in tables 1 and 2.

Tab. 1: Mineralogical data for phonolite

Compound	Average share / %
Zeolites	45,0
Alkali feldspar	31,7
Aegirinaugite	10,3
Wollastonite	9,3
Calcite	1,1
Goetzenite	1,1
Others (Melanite, apatite, titanite ...)	1,5

Tab. 2: Chemical data for phonolite

Compound	Average share / %
Si (as SiO_2)	48,2
Ti (as TiO_2)	0,4
Al (as Al_2O_3)	18,1
Fe (as Fe_2O_3)	4,1
Mn (as MnO)	0,2

Mg (as MgO)	1,0
Ca (as CaO)	8,3
Na (as Na_2O)	5,9
K (asK_2O)	5,1
P (as P_2O_5)	0,2
H_2O	6,7

The phonolite contained in zeolite is almost exclusively a so-called natrolite ($Na_2Al_2Si_3O_{10} \bullet 2H_2O$) with a pore diameter of ca. 2.6 to 3.9 angström.

Material and Methods

In order to determine the degree of separation of dioxins and furanes to phonolite, tests were done in the bypass of an incineration plant. For this the material, in a fixed bed adsorber, was charged with pre-purified flue gas from an incineration facility. The phonolite implemented was tempered before the test at a temperature of ca. 450 ^{o}C and a residence time of 0.5 h, in order to drive out the water of crystallization. The material was implemented with a grain size of 1 to 4 mm. The further test parameters are summarized in table 3:

Tab. 3: Test parameters

Temperature	110 ^{o}C
Velocity	0,12 m/s
Height of bed	0,8 m
Inner diameter of adsorber	207 mm
Volume flow	ca. 15 m^3/h

The partial volume flow was removed after a 2-staged wet scrubber at ca. 60 ^{o}C, heated up to reactor temperature and then fed to the adsorber.

The adsorber is kept at a slight underpressure by a rotating compressor downstream of it.

The PCDD/F measurements were made simultaneously over a period of 6 hours from input and output of the adsorber. Sampling was done isokinetically and following VDI Guideline 3499 Sheet 2. In total, three measurements were done, namely, after an 18 h, 42 h and 66 h charging of the phonolite with flue gas in the adsorber.

Results and Discussion

The results of the measurements are given in table 4. The total rates of separation are 99 % and higher, in the middle of the 3 measurements 99.4 %. These measurements prove the very good separation results of phonolite with respect to the PCDD/F. The isomer pattern did not thereby impair the overall separation line that can be attained. The results make it clear that the emission limit value in accordance with the 17^{th} BImSchV is clearly fallen below, being on average at 0.02 $ngTE/m^3$ in the measurements, hence at only a fifth of the limit value.

Through the tests and the results that were achieved, it could be demonstrated that phonolite possesses excellent properties with regard to PCDD/F separation. The separation results that were measured open a wide spectrum of uses for zeolithic mineral rocks in the area of gas purification. The advantages in the handling of the material, the safety technology which is not required, point towards an inexpensive alternative to the adsorbent agents used till now.

Tab. 4: Results

	Measurement #1			Measurement #2			Measurement #3		
	Input	Output	rate of sep.	Input	Output	rate of sep.	Input	Output	rate of sep.
Compound	ng/m^3	ng/m^3	%	ng/m^3	ng/m^3	%	ng/m^3	ng/m^3	%
2,3,7,8-TCDD	0.022	0.00042	98.1	0.055	0.00063	98.9	0.022	0.00033	98.5
1,2,3,7,8-PeCDD	0.034	0.0011	96.8	0.07	0.0013	98.1	0.06	0.00071	98.8
1,2,3,4,7,8-HxCDD	0.006	0.00037	93.9	0.011	0.00029	97.3	0.022	0.00019	99.1
1,2,3,6,7,8-HxCDD	0.011	0.00058	94.8	0.024	0.00055	97.7	0.042	0.00035	99.2
1,2,3,7,8,9-HxCDD	0.007	0.00041	94.0	0.014	0.00036	97.5	0.023	0.00029	98.7
1,2,3,4,6,7,8-HpCDD	0.009	0.0003	96.7	0.01	0.00018	98.2	0.047	0.00014	99.7
OCDD	0.005	0.00011	97.7	0.0041	0.000075	98.2	0.021	0.000054	99.7
2,3,7,8-TCDF	0.015	0.00038	97.5	0.058	0.00055	99.0	0.033	0.00083	97.5
1,2,3,7,8-PeCDF	0.041	0.00093	97.7	0.11	0.00095	99.1	0.097	0.00094	99.0
2,3,4,7,8-PeCDF	0.4	0.0085	97.9	0.83	0.0082	99.0	1.4	0.0064	99.5
1,2,3,4,7,8-HxCDF	0.16	0.0033	98.0	0.25	0.0026	98.9	0.77	0.0018	99.8
1,2,3,6,7,8-HxCDF	0.23	0.0027	98.8	0.32	0.0022	99.3	1.3	0.0019	99.8
1,2,3,7,8,9-HxCDF	0.1	0.00034	99.7	0.07	0.00025	99.6	0.37	0.00033	99.9
2,3,4,6,7,8-HxCDF	0.77	0.0022	99.7	0.7	0.0017	99.8	3.1	0.0027	99.9
1,2,3,4,6,7,8-HpCDF	0.34	0.00086	99.7	0.2	0.00032	99.8	1.1	0.00096	99.9
1,2,3,4,7,8,9-HpCDF	0.022	0.000045	99.8	0.011	0.000016	99.9	0.06	0.000056	99.9
OCDF	0.12	0.00013	99.9	0.059	0.000074	99.9	0.13	0.00013	99.9
Total PCDD/F	2.3	0.023	99.0	2.8	0.02	99.3	8.5	0.018	99.8