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Predicting the Operating Behavior of Ceramic Filters from Thermo-Mechanical Ash Properties

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Background and Objectives

Stable operation, in other words the achievement of a succession of uniform filtration cycles of reasonable length is a key issue in high-temperature gas filtration with ceramic media. Its importance has rather grown in recent years, as these media gain in acceptance due to their excellent particle retention capabilities. Ash properties have been known for some time to affect the maximum operating temperature of filters. However, softening and consequently "stickiness" of the ash particles generally depend on composition in a complex way. Simple and accurate prediction of critical temperature ranges from ash analysis – and even more so from coal analysis – is still difficult without practical and costly trials. In general, our understanding of what exactly happens during break-down of filtration stability is still rather crude and general.

Early work was based on the concept that ash particles begin to soften and sinter near the melting temperatures of low-melting, often alkaline components. This softening coincides with a fairly abrupt increase of stickiness, that can be detected with powder mechanical methods in a Jenicke shear cell as first shown by Pilz (1996) and recently confirmed by others (Kamiya et al. 2001 and 2002, Kanaoka et al. 2001). However, recording σ-τ-diagrams is very time consuming and not the only off-line method of analyzing or predicting changes in thermo-mechanical ash behavior. Pilz found that the increase in ash stickiness near melting was accompanied by shrinkage attributed to sintering. Recent work at the University of Karlsruhe has expanded the use of such thermo-analytical methods for predicting filtration behavior (Hemmer 2001). Demonstrating their effectiveness is one objective of this paper.

Another issue concerns the experimental detection of instability in filter behavior. Pilz was able to show nicely that softening, which for mineral ashes typically occurs above 600°C up to over 800° and coincided with catastrophic failure of the filters, also lead to a drastic jump in residual pressure drop Δp_r. According to Dittler (2001) on the nature of instability and partial regeneration of surface filters, Δp_r is however not a very sensitive nor unique operating parameter, especially for thick ceramic media. We have therefore decided to base our stability analysis on cycle duration (Fig.1), although the criterion is admittedly not rigorous, nor are 50 cycles necessarily a full indication of what might happen during many thousands of cycles.

Finally, our intent is to show that ash softening at near melting temperatures is apparently not the only phenomenon causing problems with filtration, although its impact is certainly the

"final catastrophe". There are other significant changes in regeneration at intermediate temperatures, which may lead to long-term deterioration.

Filter media, particle materials and experimental details
The data reported here were obtained with ceramic filter media of the type Schumacher Dia-Schumalith 10-20, confectioned either as standard 1.5-m candles or as 150-mm flat discs. The medium is based on a SiC body with a relatively smooth skin of mullite.

Filtration experiments were performed between 200 and 800˚C in one of two types of high temperature filtration units, depending on whether candles, flat elements or both were used. (Pilz 1996; Hemmer et al. 1999) With the exception of candles, each experiment started with a fresh element. For each temperature, the maximum pressure differential across *the cake* Δp_{cake} was kept constant from cycle to cycle. The maximum pressure Δp_{max} was adjusted for each temperature to compensate for changing gas viscosity. The dust concentration immediately upstream of the filter (5 g/m^3) and the filter face velocity (5 cm/s) were the same for all runs.

The ashes used for the work described hereunder were obtained from combustion of biomass (bark ash), and municipal waste. They were used either pure, or as mixtures of ash and sorbents. The experiments reported here concentrate on air; work with carrier gas containing SO_2, HCl and water are reported in a companion paper in these proceedings *(Removal of particles and gases (SO₂ or HCl) with a ceramic filter by addition of dry sorbents)* Key material properties are shown in Table 1.

Thermo-analytical techniques used for off-line ash characterization
Ash behavior at elevated temperatures was analyzed by dilatometer (DIL), thermo-gravimetry (TGA) and differential scanning calorimetry (DSC) as described in detail by Hemmer (2001). (For basic techniques see also Hemminger and Cammenga,1989).

The DIL determines the relative change in elongation vs. temperature of a pressed powder pellet prepared under a static pressure of max. 5 MPa. The optimal rate of temperature increase is critical for the information gained: it was determined to 10K/min.

The TGA determines relative mass change of a powder sample vs. temperature under a specific gas atmosphere. The data shown here were all obtained in air at a heating rate corresponding to 10K/min.

The DSC provides information about heat flow to or from the sample (at a fixed external heating rate equivalent to 10K/min), indicating the occurrence of endothermal (e.g. melting, decomposition) or exothermal reactions.

These techniques where used to obtain a variety of information about the particle material. The current discussion is however limited to the data shown, due to constraints of space.

Comparison of ash filtration behavior and thermo-analytical data

For bark ash and municipal waste incineration ash (MWIA) respectively, Figures 3a,b and 4a,b show the filtration data and corresponding thermo-analytical measurements. At a each

given operating temperature, a horizontal or almost horizontal series of cycle times is considered to indicate stable filtration, although not necessarily complete regeneration of the filter. Exponentially decreasing times (note the log-lin plot) are characteristic for instable cycles. This is an operational definition of stability which has proven useful, although there is obviously no sharp definition of where stability ends and instability begins.

Bark ash: As seen in Fig. 3a, cycles at 200 and 300ºC are stable. The run at 400ºC shows incipient instability, whereas the rapid decline at 600ºC is typical for the well known "catastrophic" instability leading to irreversible cake attachment on the filter elements. Interestingly however, there is an intermediate temperature range around 500ºC where filtration runs stable.

The corresponding thermo-analytical data (Fig. 3b) show a normal powder expansion for the DIL, without significant mass changes of differential heat flow up to about 325ºC, where the sample begins to contract sharply until about 440ºC, when a region of normal behavior follows. There is a good correlation with filtration behavior in the respective zones up to 500ºC. The temperature region between 325 and 440ºC corresponds to a significant endothermal heat flow as well as a mass loss, which have been associated with the removal of residual carbon (c.f. Table 1 on ash composition) from the ash (Hemmer 2001).

Filter failure at the high temperature end of operation at 600ºC is also readily correlated and perhaps explained from the corresponding thermo-analytical data: From roughly 550ºC upward, the DSC signal shows an endothermic process probably corresponding to the softening of certain ash components. This softening is associated with sintering (negative expansion in the DIL signal) and some mass loss, perhaps due to evaporation.

Stable filtration definitely comes to an end at temperatures above the onset of softening. This result corresponds well to intuition and our understanding of cake mechanics from previous work. The good correlation of several regions of negative sample expansion in the DIL data with instable filtration is remarkable. It is further supported by the appearance of an intermediate region of "metastable" operation around 500ºC where the sample resumes its normal expansion.

DSC and TGA data, when superimposed on the DIL traces, are consistent with the conclusions drawn and provide indications of the type of physico-chemical changes taking place in the sample.

Municipal waste incineration ash (Fig. 4a and b): Municipal waste is a much more complex mixture than biomass with a correspondingly broad and virtually continuous spectrum of melting/reaction temperatures in the ash. From about 400ºC upward, the DSC trace shows a series of endothermal processes involving low-melting point components. The DIL detects the ash behavior with sintering-like response beginning also just below 400ºC, with a shallow plateau around 550ºC for which there are however no filtration data. Again, the DIL trace gives the best indication of filtration stability.

Filtration behavior vs. thermo-analytical data for sorbent particles

Co-injection of dry sorbent materials along with the ash upstream of the filter is used for removal of acid components such as SO_2 or HCl, Hemmer et al (2001), Hemmer et al. (2002). Figs. 5a and b provide the respective data on cycle times and ash behavior.

The Figures show a loss of filtration stability above 200°C, with a corresponding pronounced contraction of the sample starting above 275°C. (It must be mentioned that the authors are not aware of any physico-chemical transition to explain the contraction of the powder between 275°C and 400°C.)

Around 450°C there may be metastable region, for which however there are no data. The second contraction above 470°C corresponds to incipient sintering of pure Na_2CO_3.
Interestingly, the decomposition of $NaHCO_3$ to Na_2CO_3 with its sharp calorimetric peak and mass loss between 110 and 200°C does not show up in the DIL data, nor does it affect filtration.

Conclusions

- Thermo-analytical techniques, in particular dilatometry, are useful predictive tools to identify temperature regions of instable filtration behavior.

- Beside softening at the upper end of a material's temperature range, ashes as well as sorbent materials exhibit also other, intermediate regions of instability or "metastability" with respect to filtration.

- Correlations of thermo-analytical data with ash composition are at present qualitative and need more work.

- Cycle duration appears to decrease exponentially in unstable operating modes.

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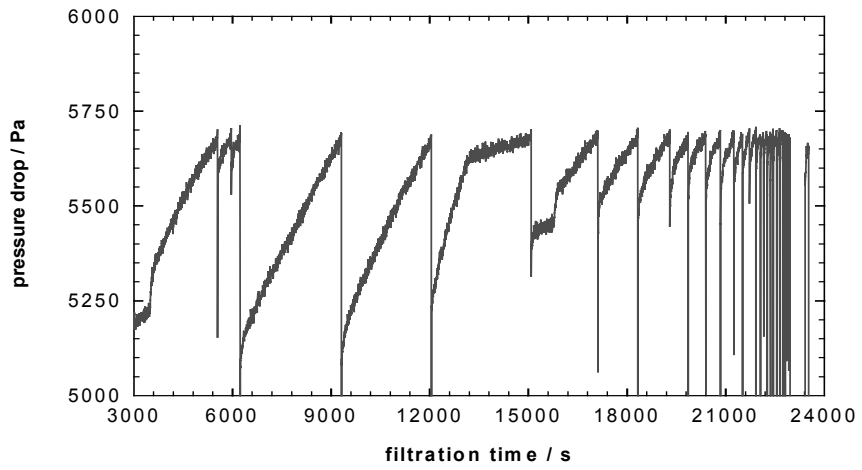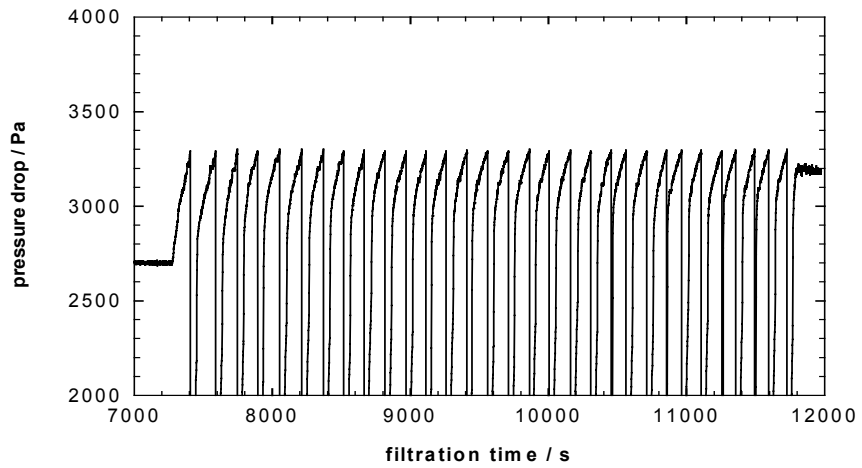
Acknowledgement

Fig. 1 - Pressure drop recorded during sequences of stable (top) or instable (bottom) filtration cycles (top: bark ash, 300 °C; bottom: incineration ash, 500 °C).
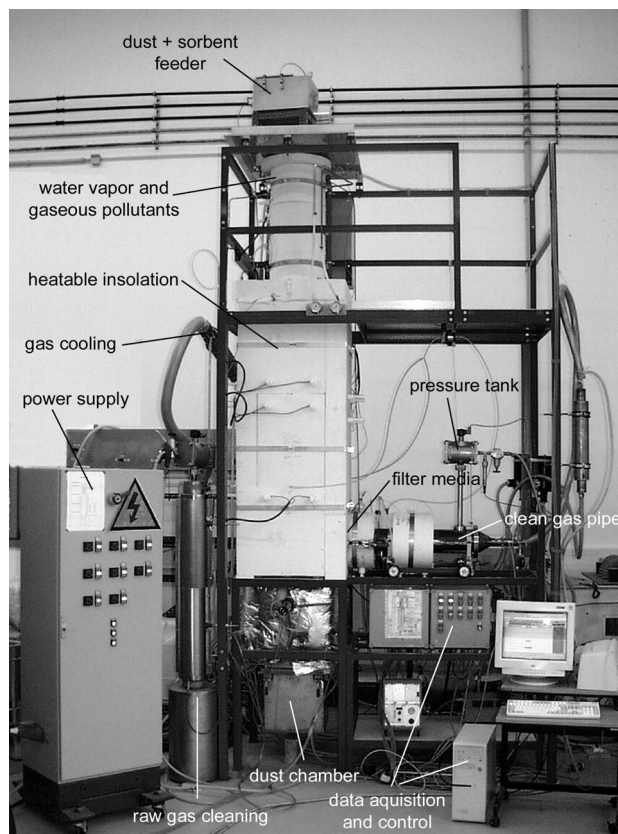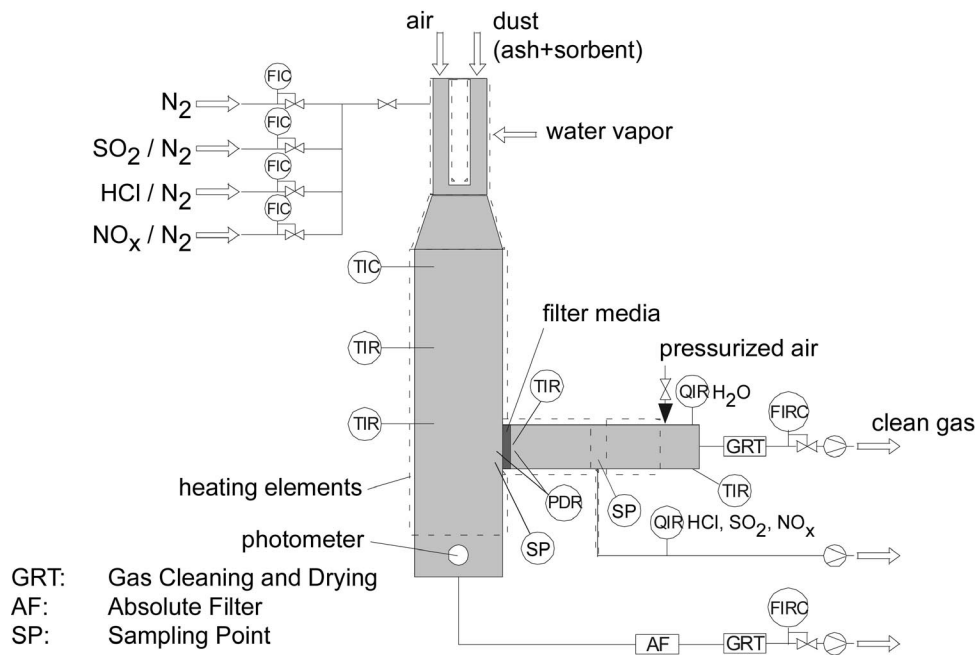
air   dust
       (ash+sorbent)

N₂

SO₂ / N₂

HCl / N₂

NOₓ / N₂

water vapor

filter media

pressurized air

clean gas

heating elements

photometer

GRT: Gas Cleaning and Drying
AF: Absolute Filter
SP: Sampling Point

Fig. 2 - High temperature filtration unit for flat disc elements. Pneumatically redispersed ash and air (plus trace gases if desired) are introduced from the top and preheated to operating temperature. Dust concentration is monitored immediately above filter disc mounted flush with the vertical main channel wall. Reverse pulse regeneration occurs from the horizontal duct (right). Δp and various control parameters are recorded continuously and used for automatic operation of the unit. Filters can be changed "hot".
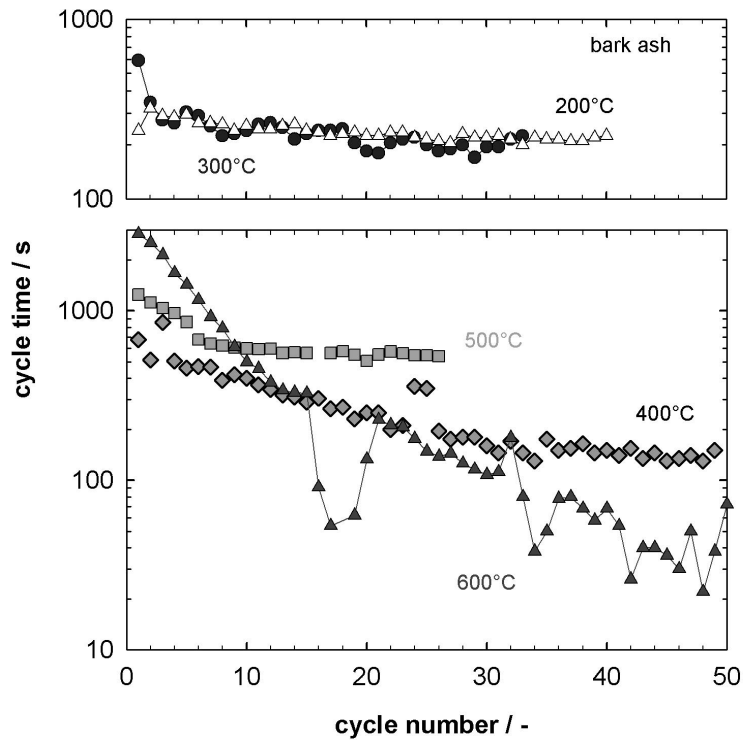
Fig. 3a - Duration (in seconds) of the first filtration 50 cycles at various temperatures for bark ash.
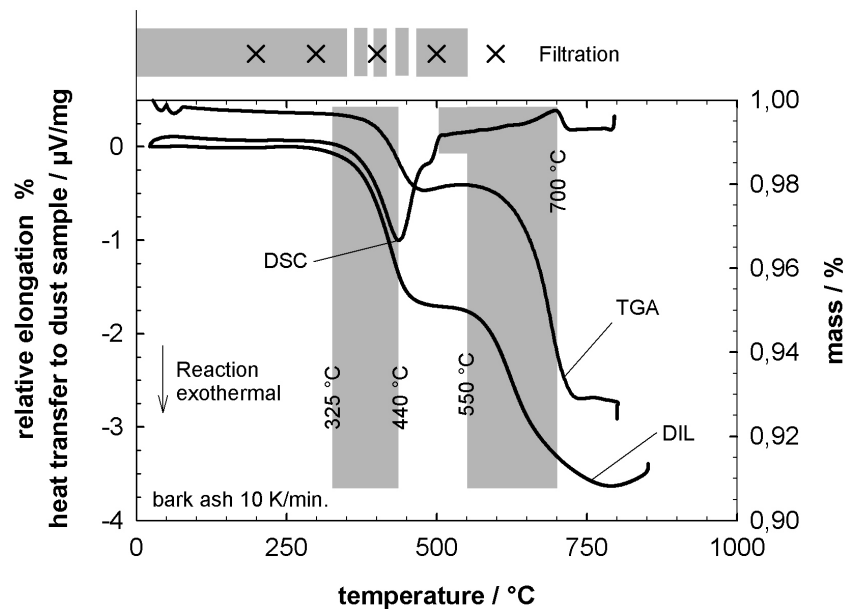

Fig. 3b - TOP: Temperature regions of stable (gray), metastable, or instable (white) filtration, X indicates measurements - BOTTOM: traces of DIL, TGA and DSC data for bark ash.
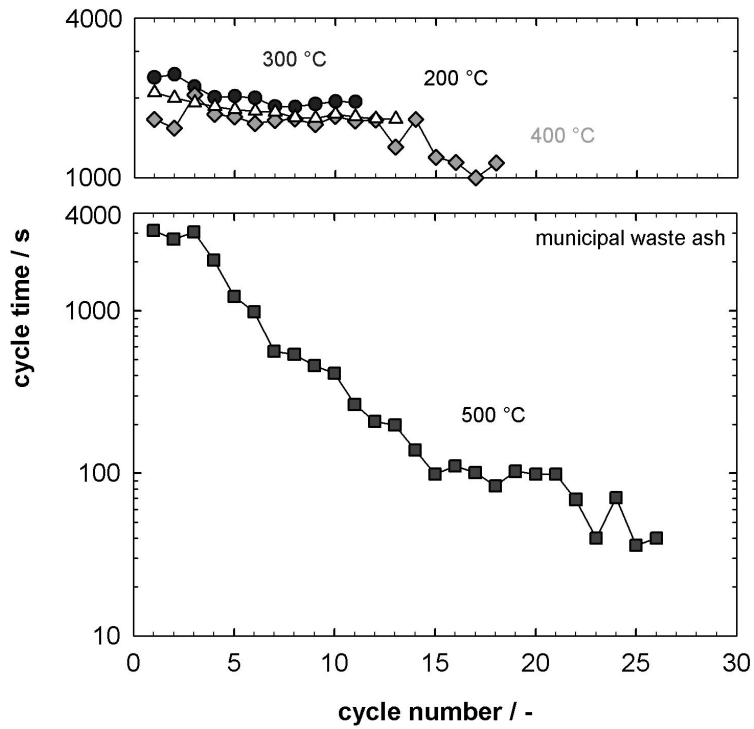
Fig. 4a - Duration (in seconds) of the first filtration 30 cycles at various operating temperatures for municipal waste incineration ash.
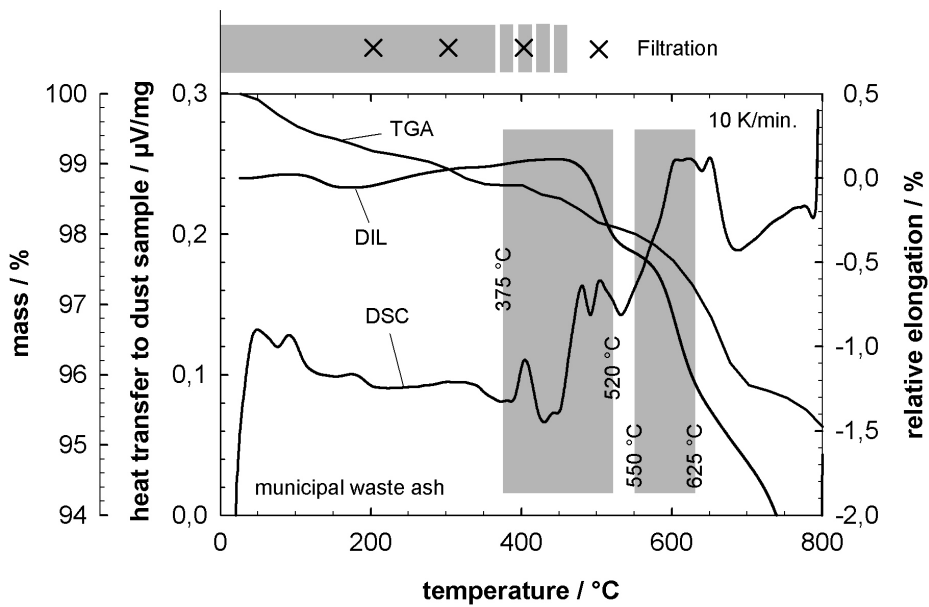

Fig. 4b - TOP BAR: Temperature regions of stable (gray), metastable, or instable (white) filtration, X indicates measurements. - BOTTOM: traces of DIL, TGA and DSC data for municipal waste incineration ash.
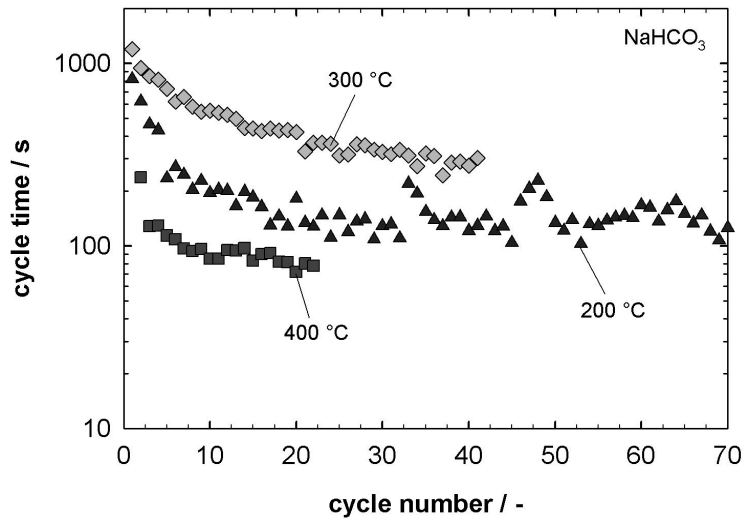
Fig. 5a - Duration (in seconds) of the first filtration 70 cycles at various operating temperatures for sorbent particles (sodium bicarbonate, NaHCO₃).
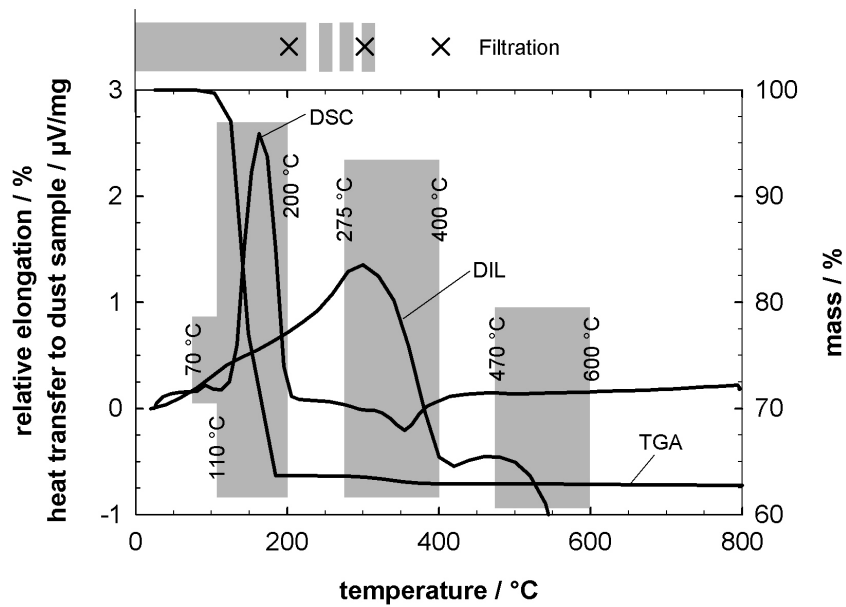

Fig. 5b - TOP BAR: Temperature regions of stable (gray), metastable, or instable (white) filtration, X indicates measurements. - BOTTOM: traces of DIL, TGA and DSC data sorbent particles.

Table 1 - Select properties of particle materials used for filtration.

	Bark ash	MWI ash	NaHCO$_3$	Ca(OH)$_2$
d_{50} / μm	23.6	53.6	21.0	3.6
BET equiv. diameter / μm	1.4	16	3.3 – 1.1	1.1
BET surface / m^2/g	11.6	3.29	4 – 12	12.49
Density / g/cm^3	2.8	2.6	2.2	2.25
Na$_2$O / wt-%	0.8	6.0		
K$_2$O / wt-%	6.0	6.0		
CaO / wt-%	27.1	31.0		
MgO / wt-%	3.3	< 2		
TC / wt-%	3.8	1.1		
Decomposition temp / °C	–	–	130	380