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Examinations of Chemical Resistance and Thermal Behaviour of Ceramic Filter Materials for Hot-Gas Cleaning

Keywords: high temperature corrosion, ceramic candle filter, hot-gas cleaning, thermodynamic modelling

Introduction

Increasing prosperity and the steady growth of the world population lead to a strongly rising energy requirement. Therefore the saving of the available resources as well as the limitation of CO₂-emission are the main reasons for developing highly efficient power stations.

The use of combined cycle technology for advanced coal fired power plants allow a significantly higher conversion efficiency than it is possible in an only steam power plant. In order to increase the gas turbine inlet temperature, the filtration of fine particles is necessary. Therefore the filtration unit is one of the key components of the circulating pressurized fluidised bed combustion technology (PFBC). To use this technology more effectively, gas cleaning at high temperatures or in an reducing atmosphere is necessary.

A possibility of the effective gas cleaning at high temperatures is the use of porous ceramic candle filters. The structure of such filter elements usually consists of a highly porous support which ensures the mechanical strength and a layer which operates as the functional part for the particle removal. To ensure a guaranteed lifetime of about 16000 h the effect of combustion or gasification atmosphere and temperature on the thermal and mechanical properties of the filter material has to be studied.

The examinations and results, described in this article, are part of some previous work. This paper focuses especially on the chemical resistance and the thermal behaviour of the used ceramic filter materials.

Objective

It is the objective of the project to develop a model for estimation and assessing the chemical resistance of ceramic filter materials under different conditions of use. Particularly the interactions between filter material and gas atmosphere as well as filter material and dust shall be taken into consideration.

Approach

In co-operation with Fraunhofer Gesellschaft, several different filter materials from both commercial suppliers as well as new developments were investigated.

- Recrystallized silicon carbide : (R)
- Oxides : Alumina (A), Spinell (S)
- Clay-bounded silicon carbide : (C)
- Liquid phase sintered silicon carbide : (L)

The materials were prepared to specimens of the size of $5 \times 6 \times 45 \text{ mm}^3$ or $6 \times 8 \times 60 \text{ mm}^3$ respectively and exposed in a simulated flue gas atmosphere (without dust). The treated specimens were examined by chemical analysis, radiographic and scanning electron microscope examinations as well as mechanical testing.

In order to assess the effect of ash components (especially alkalis) on the chemical resistance of filter materials, additional experiments were carried out.

By the comparison of the experimental results with the thermodynamic data, a model in order to estimate the resistance of filter materials under different conditions of use is strived for.

Project Description

The examinations were carried out in two different ways. On the one hand material exposure in experimental plants (electrically heated flow reactor and natural gas fired reactor respectively) took place and on the other hand thermal analytical examinations were carried out.

In the flow reactor the specimens were exposed to a simulated gas atmosphere, oxidizing or reducing respectively (without dust). For the exposure, a typical gas composition of brown coal combustion or partial gasification were chosen (table 1). The experiments were carried out for a period of one hundred hours. About a vaporizer unit alkalis were added to the gas stream. After finishing the experiment, the specimens were examined by structural analysis as well as mechanical testing. The results of the mechanical testings are reported in [Westerheide, 2002]. A summary of the tests carried out in the reactor is given in table 2.

In the natural gas fired reactor the materials were used in form of cut-down candle filters. By conditioning the gas atmosphere a brown coal combustion could be simulated. Additionally ash were added to the gas stream. The experiments are still going on, so that no current results can be presented.

Parallel to experimental works, the thermal behaviour of the materials was analysed with the help of thermal analytical examination methods like differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) and mass spectrometry (MS). Using the DSC-equipment the switching from a quantitative DTA and DSC rod version to a DROP DSC version is possible. The advantage of the DROP DSC version is the bigger sample container, which makes it possible to use the specimens as a piece and not as powder.

Before thermal treatment the materials have been prepared in a special way. Depending on the used measuring method the specimens either were soaked with different solutions or the grinded filter materials were mixed with the substances to be examined. These specific tests of selected materials shall indicate a possible corrosion attack of the filter materials by ash components, especially alkalis.

The got results will be compared with thermodynamic data. With the help of ChemSage to calculate the thermodynamic equilibrium, different variations of process conditions as well as ash compositions will be examined.

Results

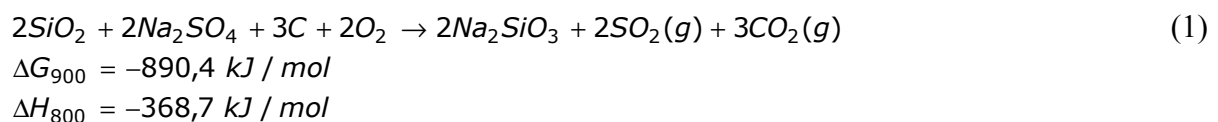
The represented results refer to the examinations regarding the thermal behaviour of selected filter materials.

Starting point of the examinations was the thermal behaviour of the unchanged clay-bounded materials. Starting out from the elementary composition of the filter materials thermal effects has to be expected in the temperature range of the melting point of ashes. Figure 1 shows the thermal behaviour of the C1 material measured with the DSC-equipment. In the temperature range from 850 °C to 1000 °C there is an endothermic effect due to the melt of parts of the binding phase. The comparison with the elementary composition and the phase diagram (figure 2) confirm this. The composition of the materials C1, C2 and C3 is potentially in a critical area of low melting eutectoid mixture. Only the material C4 is out of this area. A comparison of the clay-bounded materials with respect to the elementary composition shows the reason for this. The C4 material has a smaller amount of potassium, a little higher amount of calcium and a large amount of magnesium (figure 3). This leads to a very stable phase composition.

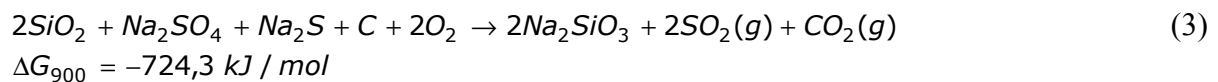
In order to assess the effect of ash components (especially alkalis) on the chemical resistance of the filter materials, additional experiments with treated materials were carried out. The specimens were soaked with sodium-sulfate or potassium-sulfate respectively.

As expected, for the oxides A and S only the melting point of sodium sulfate at 884 °C was measured. This can be confirmed by thermodynamic calculations. For the material L1 the results are shown in figure 4. In both cases a strong exothermic effect above 700 °C could be detected. A TG-analysis in combination with mass spectrometry was carried out in order to identify the formed gas species. As figure 5 shows, the reaction is accompanied by a weight loss and the formation of the gaseous products CO₂, SO₂ and a low content of COS. Due to the formation of gaseous components the theoretical weight loss through the reaction with Na₂SO₄ amounts 5,3 weight-%. The measured weight loss amounted 4,3 weight-%.

Remarkable is the fact, that the effect appears still below the melting point of the respective salt. From the thermodynamic point of view the existence of excess carbon for a reaction between the alkalis and the silica is necessary.



A possible sequence for this reaction could be the following.



Reaction (2) is known from the production of sodium-sulfide [Fischer, 1982]. In the binary system Na₂SO₄ – Na₂S exists a eutectoid mixture at a temperature of 730 °C and about 23 weight-% of sodium-sulfide (figure 6). Therefore the complete conversion of sodium-sulfate will be prevented, so that reaction (3) might be possible. The exothermic effect, the gaseous products and the initial temperature of the reaction indicates such a mechanism.

In [Jacobson, 1993] similar results were reported. However, it was assumed, that sodium-sulfate was in the liquid state. The differences between sodium- and potassium-sulfate are the initial temperature of the reaction and the intensity of the exothermic peak. The former is due to the different melting points and the different activities of the alkali salts.

In comparison to the R-materials in principle the same effect was detected. Only the intensities of the exothermic effects are different. A dependence of the amount of excess carbon was assumed, so that an analysis of the content of excess carbon was ordered. At such an analysis the sample will be heated under oxygen atmosphere and the formed CO₂ will be detected by means of infrared spectroscopy. But the analysis don't confirm this assumption. The content of excess carbon has no influence on the intensity of the measured peaks.

The importance of the excess carbon were examined in further investigations. So the procedure of soaking, drying and thermal treatment were replayed four times at the same sample. The results of the DSC-measurements are given in figure 7. After the first measurement during the 2nd soaking the outer layers of the specimen began to crumble. That indicates the formation of soluble silicates (Na₂SiO₃ and Na₂Si₂O₅ respectively). Figure 8 shows the process of disintegration in a chronological sequence. The formation of sodium-metasilicate and sodium-disilicate were also shown with thermodynamic calculations.

Before treatment and after the last measurement the content of excess carbon of the sample were analysed. The results show the effect of the treatment. The content of excess carbon before and after treatment is nearly the same, but the beginning of the attack of the SiC differs seriously. The initial temperature of burn off the SiC changes from 1000 °C before treatment to 700 °C after treatment. The curve of the heat flow of the fourth measurement in figure 7 confirm these results.

The thermal behaviour of the clay-bounded materials (C) is different to the others (figure 9). Below the melting point of sodium-sulfate there is no exothermic effect. As in the case of the measuring of the untreated material C1 there is an endothermic peak at a temperature of 850 °C (material C3). It follows the endothermic peak of the melting point of Na₂SO₄. Above a temperature of 900 °C the expected exothermic effect was detected.

The SiC grain is enclosed completely with clay. It has to be suspected, that this works as a protective layer, so that the sodium-sulfate can not react with the SiC as long as the layer is intact. The melt of the sodium-sulfate as well as the formation of different molten phases itself leads to a destruction of the protective layer. As a result the mechanical strength of the support material decrease.

In the flue gas of a power station not only sodium-sulfate is present. A mixture of different forms of alkalis exists, so that the formation of low melting phases is possible. For this reason examinations with a mixture of sodium-sulfate and sodium-chloride were carried out. Above a temperature of 625 °C a eutectoid mixture was calculated. It can be assumed, that the liquid alkalis dissolve the protective silica layer and the SiC will be attacked at lower temperature.

Figure 10 shows the result of the DSC-measurement for the R-material. The endothermic effect at 630 °C is due to the melting point of the eutectoid mixture. Already at a temperature of 730 °C the beginning of the exothermic effect can be detected. In comparison, at the same material mixed with pure sodium-sulfate the exothermic effect starts at 800 °C.

The same examination like the R material were carried out with unsintered raw material (SiC grains with silica layer). The differences are clear (figure 11). The thermal behaviour of the raw material mixed with pure sodium-sulfate meets the expectations. The exothermic effect appears after the sodium-sulfate is molten. This is due to the destruction of the protective layer. The other mixture leads to a displacement of the exothermic effect to lower temperatures. This indicates, that the formation of low melting phases influence the resistance of the materials.

The examinations in the DSC-equipment as well as in the analytical TG-analyzer (STA-TG) were carried out under neutral nonreactive atmosphere. In order to assess the differences to a reducing or oxidizing atmosphere soaked specimens were exposed in a thermal gravimetric analyzer for reactive gases. By means of a gas conditioning unit the required gas composition could be adjusted (table 2).

The comparison of the specific weight changes for two materials are given in figure 12 and figure 13. Remarkable is the congruence of the weight changes in reducing atmosphere and the STA-TG-equipment. The thermal behaviour seems to be the same. Conspicuous is the weight loss at higher temperatures in oxidizing atmosphere. In order to identify the causes for the different behaviour thermodynamic calculations were carried out. The result for the stoichiometrical input in accordance with equation (1) is given in figure 14 a. In a temperature range around 800 °C the formation of silicates is probably. The influence of the partial pressure of the product gas SO₂ is shown in figure 14 b. Almost over the complete range of the fugacity of SO₂ the formation of meta-silicate is possible. However, if there is an excess of oxygen with respect to the stoichiometrical composition, the formation of silicates is forced back (figure 14 c). The results of the variation of oxygen partial pressure in the product gas shows the strong effect of oxygen (figure 14 d). In practice, the formation of soluble silicate under oxidizing conditions is not probably and the suggested reaction doesn't take place. Therefore the weight loss at higher temperature presumably is due to the melt of sodium-sulfate. The exact correlations between the material behaviour and the kind of atmosphere still must be examined.

Conclusions

Although the examinations are not completed at present, the previous results indicates different behaviour with respect to the material on the one hand and with respect to the gas atmosphere on the other hand. Concerning the chemical resistance of the filter materials reducing conditions are more critical as oxidizing conditions.

A critical point for the use of ceramic filter materials is the upper operating temperature. Melting has to be expected in the temperature range above 800 °C. That involves a degradation in strength and may lead to the damage of the candle filters. Maybe a limitation of the operating temperature for the used filter materials is necessary.

Further investigations are needed to show the dependence of the composition of real process gases (combustion or gasification respectively) concerning the chemical resistance and the thermal behaviour of the used filter materials.

Future Activities

The immediate focus of the project are examinations to the interactions between ash components and the filter support material. Using ChemSage to calculate the thermodynamic equilibrium the dependence of the chemical resistance of the gas composition shall further be examined. New examination methods like high temperature microscopy, in which reactive gas environments can be adjusted, shall be carried out.

References

Westerheide, R. et al. 2002. Effect of Combustion Conditions on Properties of Ceramic Hot Gas Filters. *Proceedings Paper of the 26th Annual Conference on Advanced Ceramics & Composites*, Cocoa Beach, Florida

Jacobson, N. S., 1993. Corrosion of Sillicon-Based Ceramics in Combustion Environments. *Journal of American Ceramic Society* 76(1):3-28.

Fischer, H. and Mayer, D., 1982. Schwefelwasserstoff. *Ullmanns Encyclopedia of technical chemistry* 21: 167-178.

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Figures and Tables

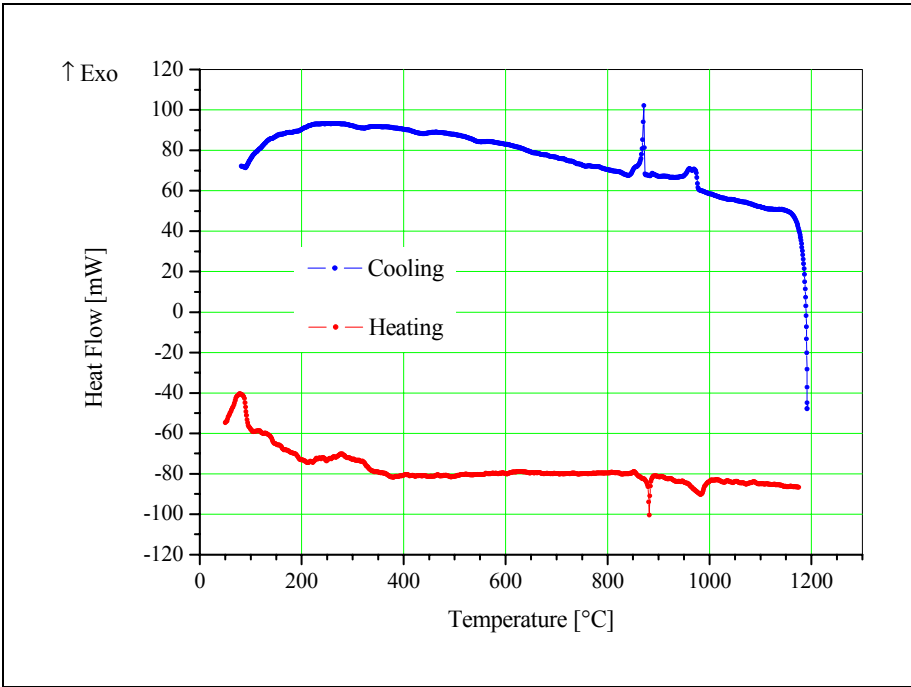


Figure 1 Thermal behaviour of unchanged clay-bounded material C1

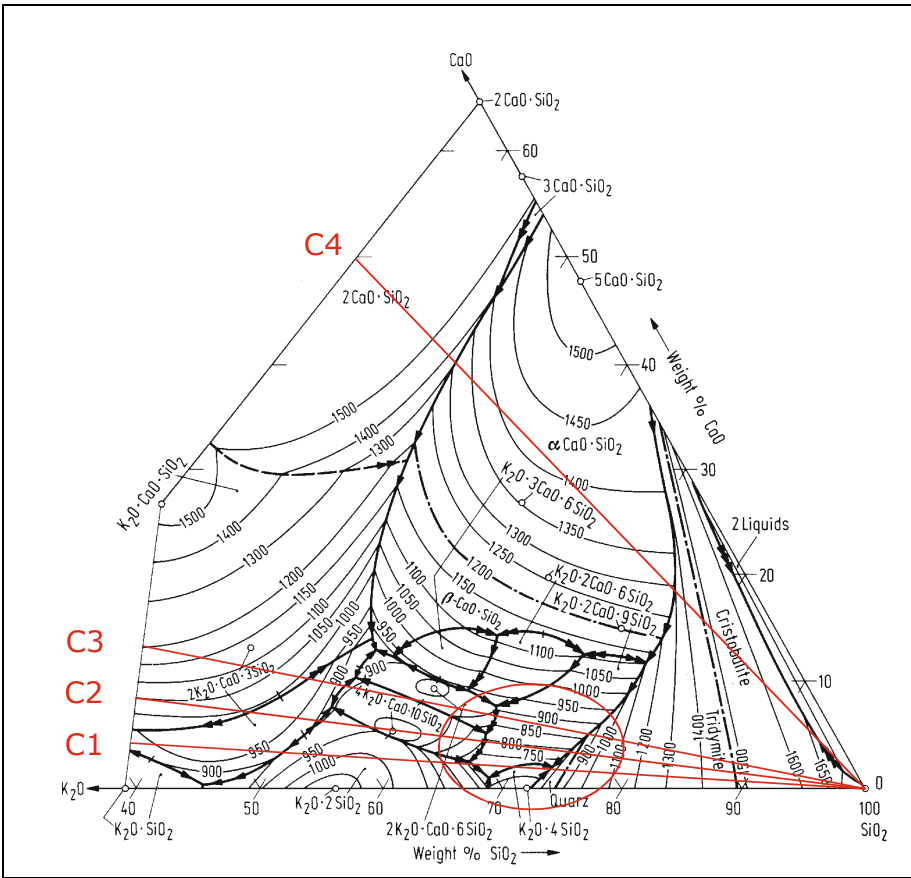


Figure 2 Phase diagram of the System K₂O-CaO-SiO₂

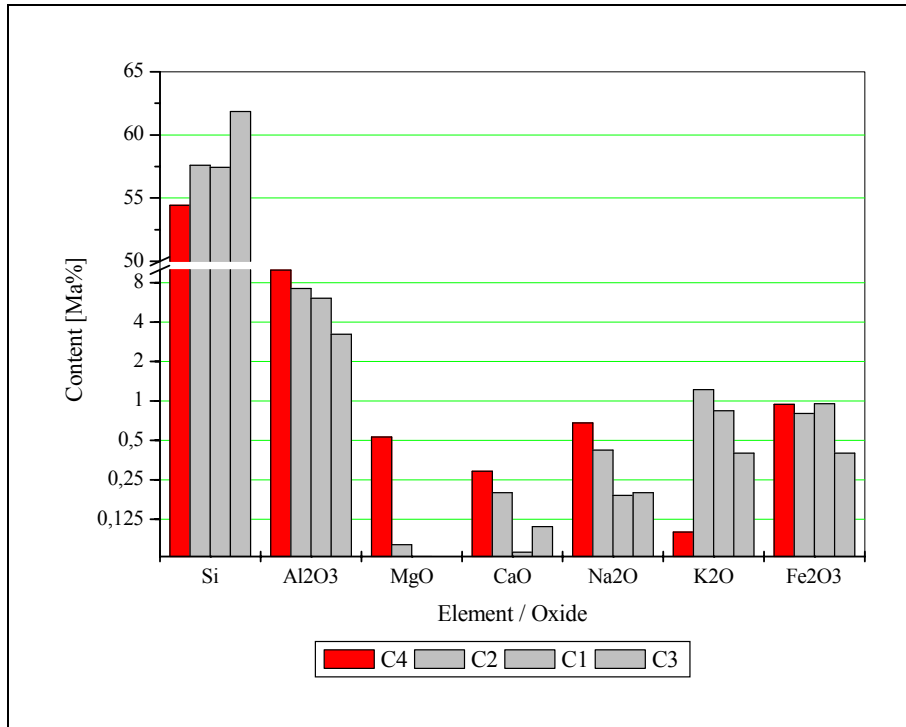


Figure 3 Comparison of the elementary composition of the clay-bounded materials

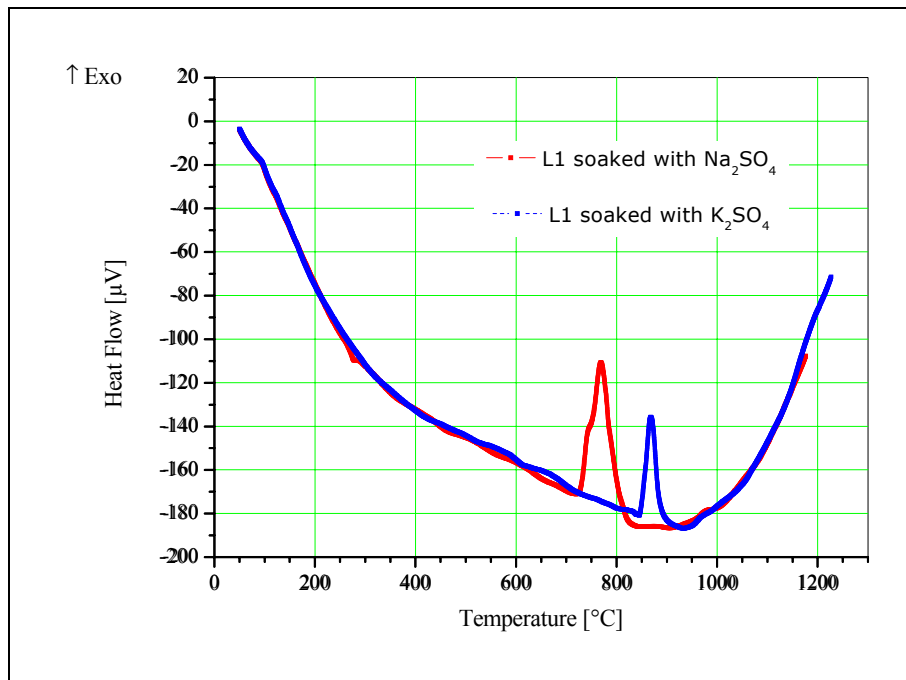


Figure 4 Thermal behaviour of the L1 material soaked with Na_2SO_4 or K_2SO_4 respectively

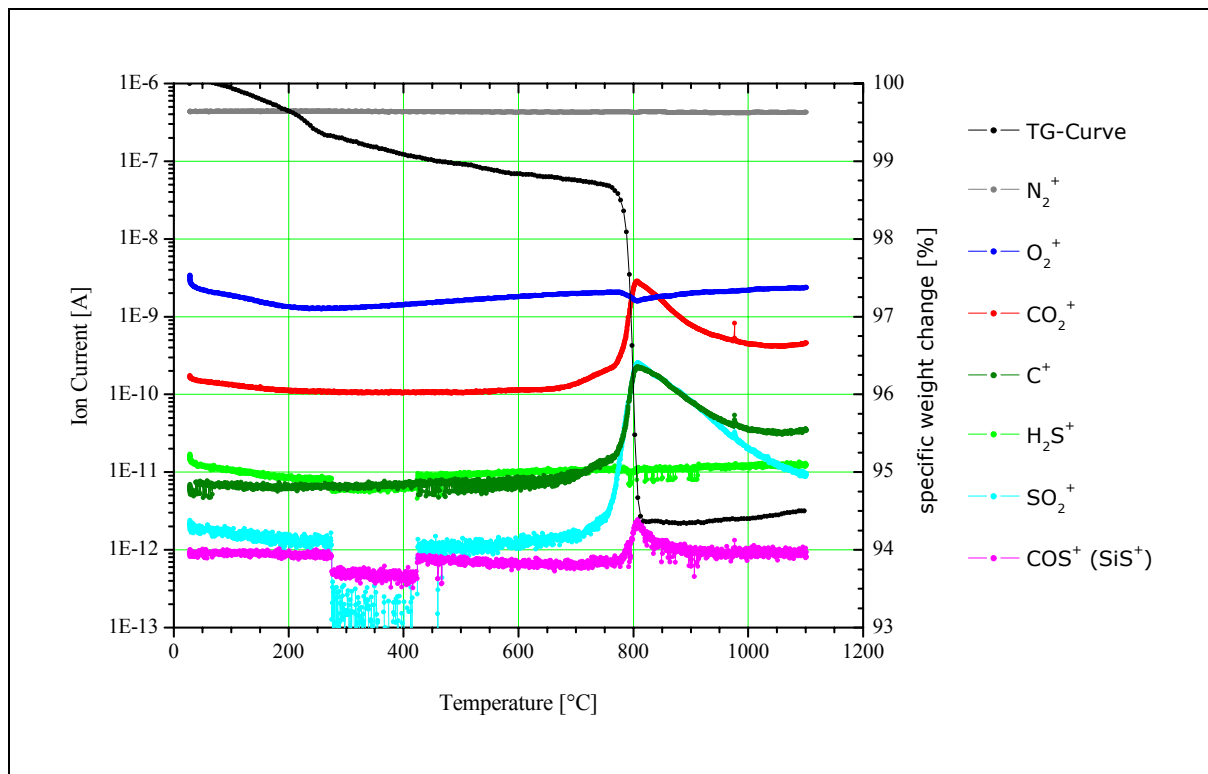


Figure 5 TG-analysis and the formation of gaseous products

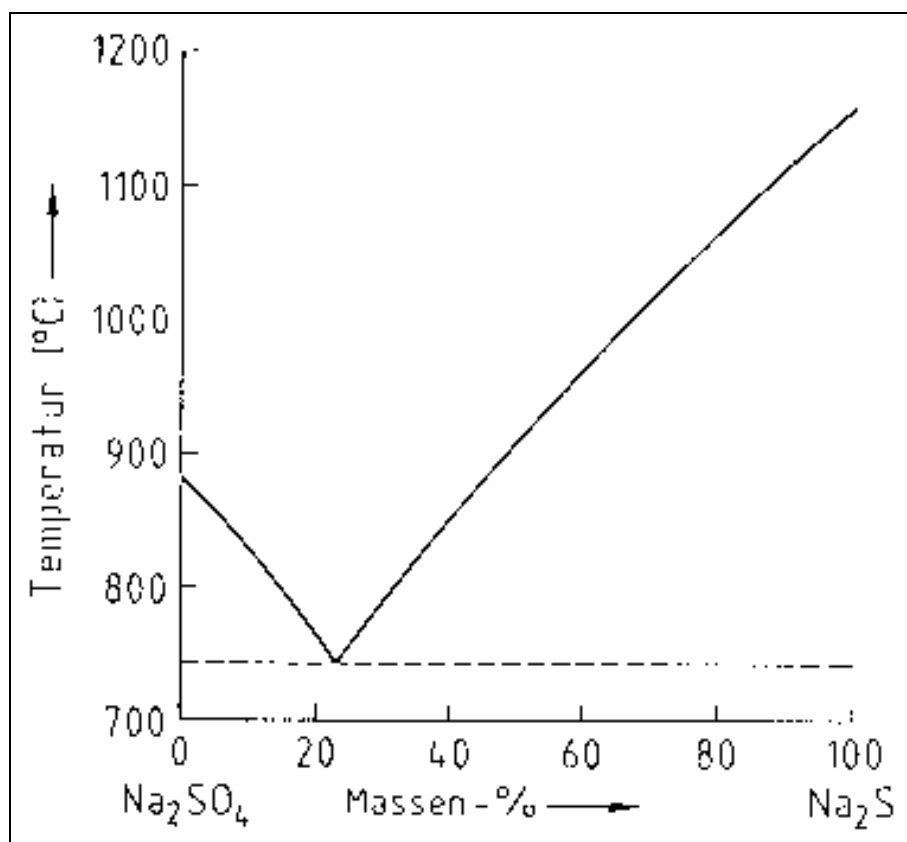


Figure 6 Phase diagram of the System Na₂SO₄-Na₂S

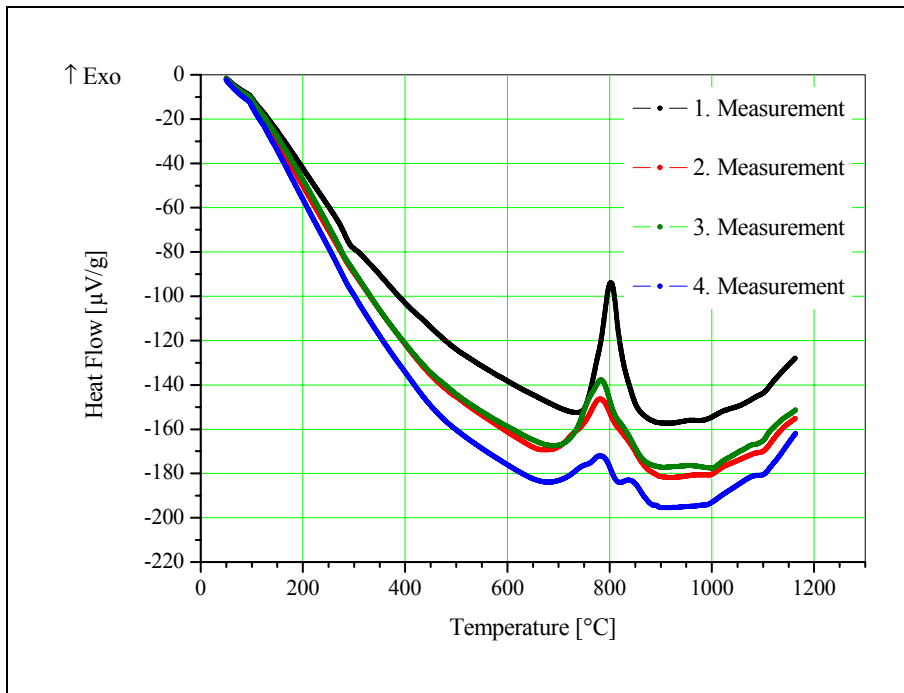


Figure 7 Comparison of the measurements with replayed soaking

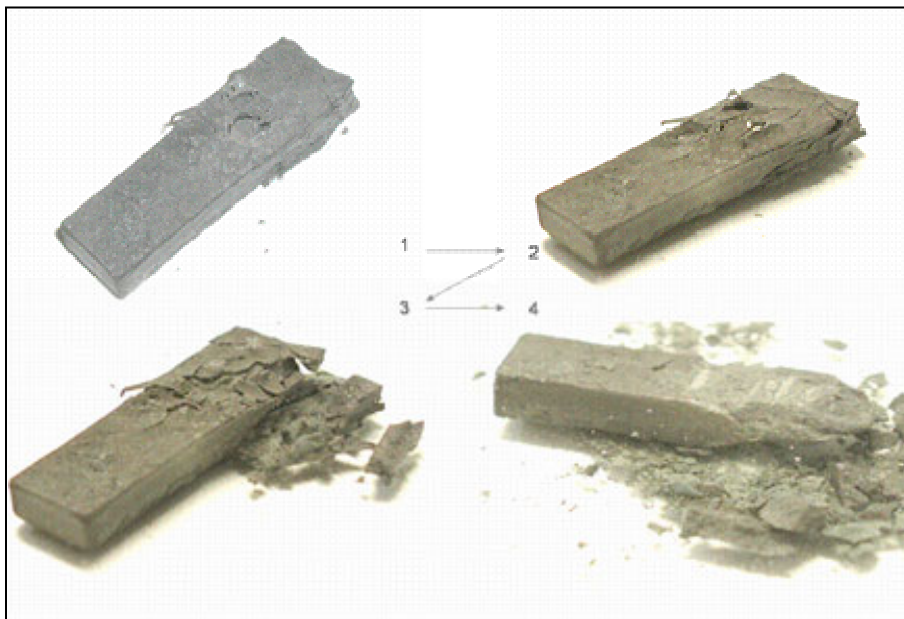


Figure 8 Process of disintegration of material L1 in a chronological sequence

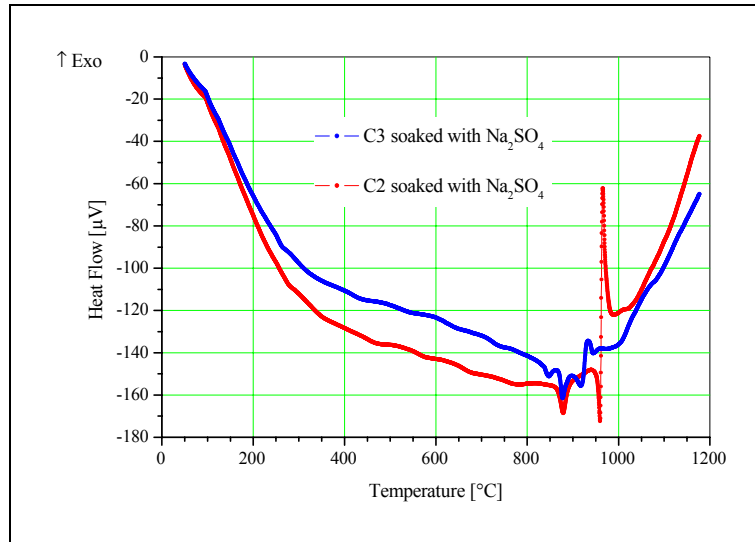


Figure 9 Thermal behaviour of the clay-bounded materials C2 and C3

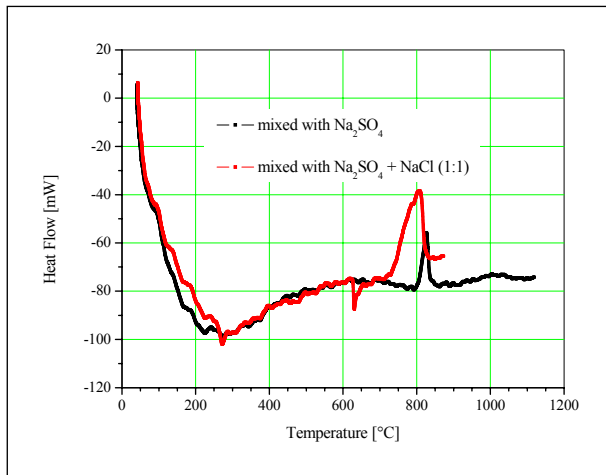


Figure 10 Comparison of the thermal behaviour of the material R mixed with different alkalis

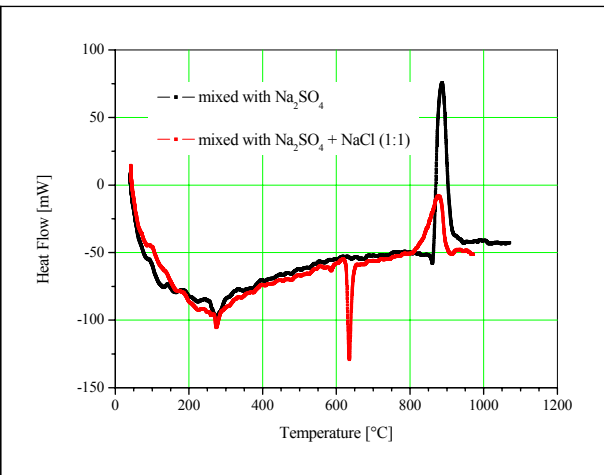


Figure 11 Comparison of the thermal behaviour of the raw material mixed with different alkalis

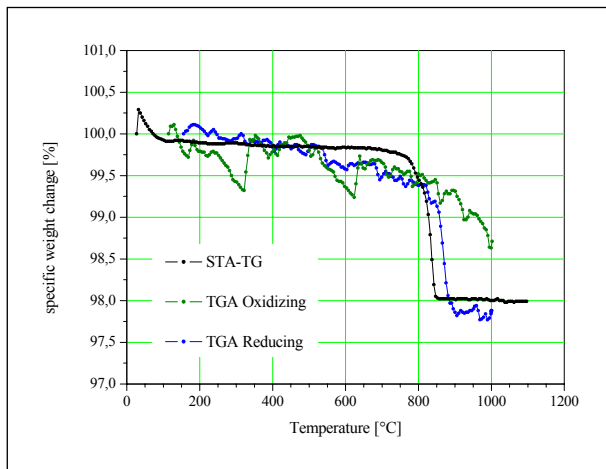


Figure 13 Comparison of specific weight changes of the C1 material in different gas compositions

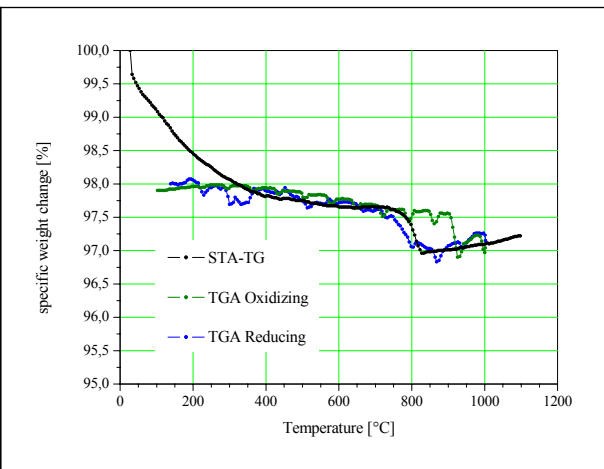


Figure 12 Comparison of specific weight changes of the R material in different gas compositions

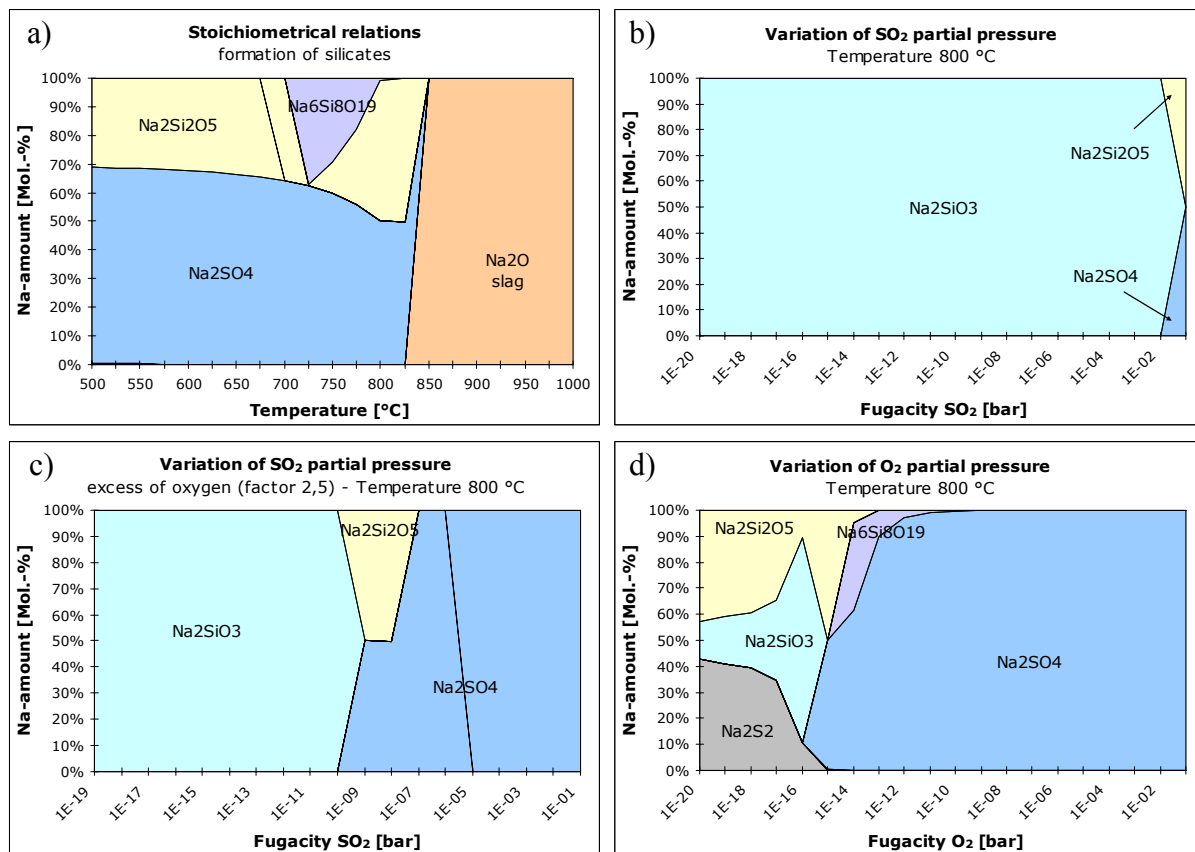


Figure 14 Results of the thermodynamic calculations (formation of silicates)

Table 1 Gas composition for reducing and oxidizing atmosphere

Component	Gasification	Combustion
	Reducing [Vol-%]	Oxidizing [Vol-%]
N ₂	63	68
CO ₂	15	14
O ₂	-	3
H ₂ O	14	15
CO	4	-
H ₂	4	-

Table 2 Tests carried out in the flow-through reactor

No.	Atmosphere	Temperature [°C]	Pressure [MPa]	Alkali load
1	Reducing	400	1	No
2		650	1	No
3		650	1	Yes
I*		750	0,5	Yes
4	Oxidizing	850	0,5	No
5		750	0,5	Yes
6		850	0,5	Yes
II*		850	0,5	Yes

* Experiments carried out with soaked specimens