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CERAMICS – NEW APPLICATIONS IN A TRADITIONAL FIELD OF THERMAL ANALYSIS

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Ceramics is by tradition one of the main fields of application for methods of thermal analysis. Changing technology and environmental problems have provided new reasons for the extensive use of highly-developed TA instrumentation. It is shown that TA can solve difficulties in production processes, provide new information for the optimum use of raw materials and select further fields of application for ceramics.

What does the term ceramics mean? Ceramics is a collective denomination for pottery, building and raw materials mostly of silicate, relatively high-melting substances which are formed at ambient temperature and heated for solidification to about 900-2000°. Ceramics therefore includes the materials and the production technologies. The tradition of pottery and building ceramics can be traced back to early history of mankind. Hence, ceramics belongs to the oldest techniques of all.

In contrast, thermal analysis has a comparatively very short past. In the historic development of thermal analysis, however, a close connection with ceramics can be found, as DTA and dilatometry were early applied for the testing of raw materials.

More than for other fields, ceramics as a high-temperature technology offered ideal conditions for the use of thermal analysis, due to the very typical behaviour of many clay minerals during heating. Table 1 outlines various points of contact between ceramics and thermal analysis, in a loose historical sequence.

Table 1

Connections between ceramics and thermal analysis

Ceramics		Thermal analysis
High-temperature technology	↔	Temperature-dependent analytical methods
Manual production		
↓		
Industrial mass prod.	↔	Single TA methods
↓		DTA
Raw materials control	↔	TG
		Dilatometry
↓		↓
Increased quality demands	↔	Simultaneous thermal analysis
↓		↓
Replacement of natural raw materials		
↓		
New production technologies	↔	Faster TA systems
↓		↓
		Automatization
		↓
	↔	Process control
↓		↓
New applications for ceramic materials	↔	Research

New problems for ceramic materials in the field of environmental protection as well as information from the simultaneous use of TA methods in combined units result in new applications of thermal analysis in ceramics. Here a few examples of interesting problems for TA are discussed.

EXPERIMENTAL RESULTS

Investigations of ceramic raw materials are strongly correlated with the corresponding production technology and are of great economic importance for highly-mechanized mass production /tableware, porcelain, floor and wall tiles, sanitaryware/. Thus, the role of the investigation of raw materials has changed from the means of finding the cause of damage in a product to the means of avoiding any breakdown in production.

The development of thermoanalytical instrumentation during the past two decades has led to equipment which is adaptable to changed technologies, or which yields new information on known material systems. The introduction of the fast-firing method, above all for the production of tiles, showed that kaolin behaves very differently during short heating times [1].

The dehydration of kaolinite at about 500-700^{o} extends over 5.5 min at a heating rate of 50 degree/min; at a heating rate of 4 degree/min the corresponding reaction lasts 33 min. In a fast-firing technology, the reactions in a ceramic mass proceed with considerably higher momentary energy consumption or release in comparison to the conventional firing process.

In DTA systems with low thermal inertia an optimum raw material selection can be met. For this application a new DTA system heated by a simple halogen lamp can be successfully used.

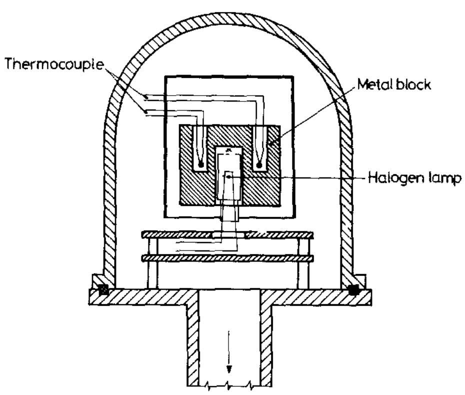

Fig. 1 Scheme of the radiation-heated DTA system 404 R.

A metal block takes up the radiation heat from the halogen lamp, which gives a heating system with very low thermal inertia and a minimum power consumption of 100 W up to 800°. Small glass or quartz glass tubes hold samples and thermocouples. At the high heating rates possible, up to 100 degree/min, the good peak resolution is of great advantage /Fig. 2/.

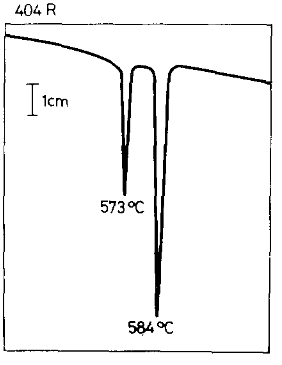

Fig. 2 Separation of peaks of the endothermal crystal transitions of quartz and potassium sulfate. SiO_2 10 mg, K_2SO_4 5 mg, 10 degree min^{-1}, air, DTA 4 μV/cm.

The supplementary information of evolved gas detection /EGD/ becomes of value in the diagnosis of waste products in a brick factory. Dilatometry alone could not give a sufficient explanation for the failure, in contrast with the situation with additional simultaneous EGD with a gas density detector /Fig. 3/.

In this way, the correlation between unexpected changes in length (see also the derivation of the length curve D/L) and gas emission can be established. In this case high contents of $CaCO_3$, clearly shown by gas detection with a gas density balance in the poor quality raw material, were the cause of the appearance of cracks in the bricks after firing. With changes in the raw material components, due either to inhomogeneities in natural occurrence or to the conscious admixture of foreign materials to the clay mass, TA can also provide information on the necessary adaptation of the firing process. This could be followed with quantitative DTA /DSC/ by admixing settling mud to a brick clay mass on a commercial scale. The energy arising from the combustion of the organic carbon in the mass was determined and considered for the adjustment of the firing curve in the production furnace.

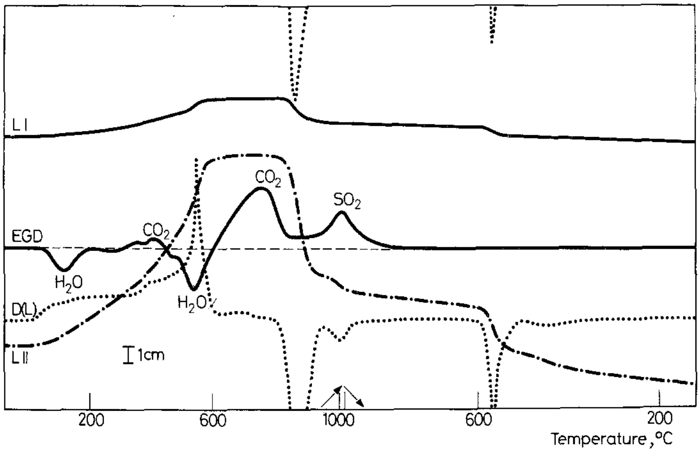

Fig. 3 Simultaneous dilatometry-EGD experiment on brick raw material. Sample: unburnt brick, l_o: 43.05 mm, sample holder: quartz glass, heating rate: 5 degree min^{-1}, LI: 5000 µm, LII: 1000 µm, D/L/: 50 µm/min, atmosphere: air 6 l/h.

The extensive characterization of kaolin, via the kinetics of the dehydration reaction, has become of interest for the use of this material for ground layers at large dust heaps /to keep toxic materials away from ground water circulation/.

DTA /STA/ tests on ancient bricks, terra cotta, mortar and other building materials show that these can furnish authoritative information on the state, composition, prehistory and susceptibility to weathering, which facts are of technical interest and also of important value to curators of ancient monuments [2]. Mass spectrometry /MS/ is a very helpful tool for trace analysis in this field.

Gypsum, $CaSO_4 \cdot 2H_2O$, a ceramic product which seems to be relatively simple, has gained an important position in the modern building industry. During thermoanalytical tests to characterize technical gypsum products, the dependence of the reaction behaviour on water vapour has hitherto always given rise to considerable experimental difficulties. A test program was developed in our laboratory, enabling within a short time an almost complete analysis of the different gypsum modifications in TG-DTA-DTG experiment in a saturated water vapour atmosphere [3]. As compared with the commonly-used chemical-technological analysis of gypsum, an approximately 50-fold time-saving results.

The capability of a simultaneous TG-DTA mass spectrometer analysis for the research of new raw material resources is proved by the investigation of natural alunites from Italy. Nowadays, there is a renewed interest in alunite, $KAl_3/SO_4/_2/OH/_6$, a hydrated aluminium and potassium sulfate mineral, which in general is associated with clay minerals of the kaolinite and halloysite group, because it can be used as a raw material for Al_2O_3 extraction. Its industrial applications to date have been as a mordant in dyeing textiles, in paper-making and in the pharmaceutical industry [4].

The mineral samples /sodium-substituted alunites/ were analyzed to 1300^o in air corresponding to the given test parameters in the NETZSCH STA 429 combined with a Balzers QMG 511 [5,6].

The mass spectrometric information about the start of gas emission as well as the simultaneous emission of different gases is a necessary condition for the process development of Al_2O_3 extraction.

The emission of sulfur dioxide from power plants burning fossil fuels has reached environmental-destroying dimensions. According to recent press reports in Germany, a yearly quantity of 3.5 megatons SO_2 is emitted in the fuel gases /besides important quantities of nitrogen oxides, hydrogen chloride, hydrogen fluoride, carbon monoxide, as well as organic substances/. As power station firings /in contrast to industry firings/ can emit only fuel - specific harmful materials, a double field of application for thermal analysis is offered here:

1. Exact characterization of fuels /see coal analysis: approximate analysis for example in STA-MS instruments/; and

2. investigation of effectiveness of fuel gas additives for the absorption of harmful substances.

For dry fuel gas purification the easily available ceramic raw material lime, in its different forms /CaO, $CaCO_3$, $Ca(OH)_2$/, and dolomite have found a very promising new field of application. The absorptive association to fuel gas additives is a

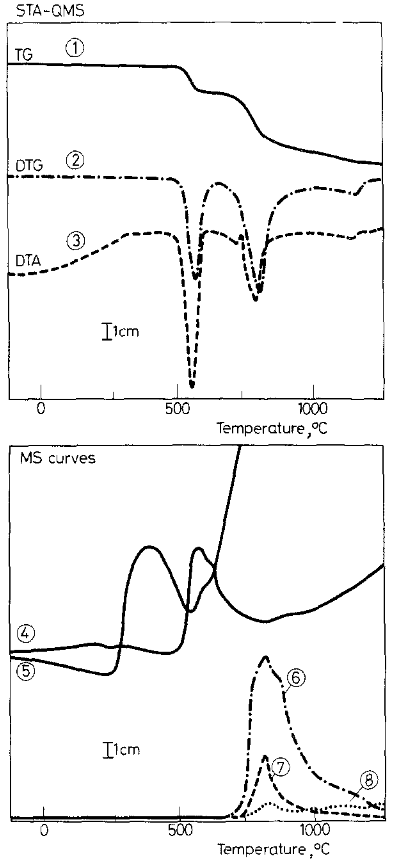

Fig. 4 Simultaneous TG-DTA-DTG-MS experiment on an impure alunite sample. Alunite 3. 69% potassium, 31% sodium, weight: 100 mg; heating rate: 10 degree min^{-1}, atmosphere: air. (1) 5 mg/cm, (2) 0.25 mg/min.cm, (3) 8 µV/cm,

	m/e	range
(4)	18 /H_2O/"	10^{-9} A auto
(5)	44 /CO_2/$^+$	10^{-11} A
(6)	64 /SO_2/$^+$	10^{-9} A auto
(7)	48 /SO_2/$^+$	10^{-10} A
(8)	80 /SO_3/$^+$	10^{-12} A

heterogeneous gas - solid reaction. The effectiveness during dry gas purification is determined by the reaction area of the solid, the partial pressure of the gaseous components of the harmful substance, the temperature and the maximum reaction time due to the fuel gas rate. Thermal analysis can be offered as an optimum test model, because it allows a wide variation of the parameters. The fuel gas temperatures are mostly considerably below 500^{o}, so that a high reaction area, as obtainable for example with $Ca/OH/_2$ by controlling the hydration process, must be available on the absorbing material. The reaction areas resulting in thermal decomposition /for $Ca(OH)_2$ above 500^{o}, or for $CaCO_3$ above about 750^{o}/ cannot be used in practical application /dry gas purification/ because of the high temperature. Some attention is being paid to the fluid bed combustion of coal by direct desulfurization with lime at high temperatures.

The corrosion problems for the apparatus by a SO_2-containing and possibly humid atmosphere can be well controlled in thermobalances by a top-loading sample arrangement. Experimental attention must be directed to the question of the reaction degree /absorbing effectiveness/ under different test conditions.

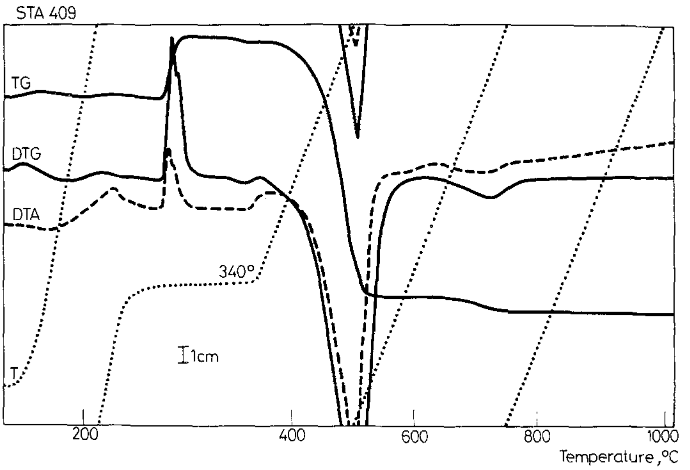

Fig. 5 Model experiment for SO_2 absorption by $Ca/OH/_2$. Sample: $Ca/OH/_2$ 79.3 mg; heating rate: 10 degree.min^{-1}, atmosphere: air 160 cm^3/min + 3.75% SO_2 above 340^{o}.

The SO_2-containing sample atmosphere leads at 340° to 8% conversion of $Ca/OH/_2$ to sulfite. /According to Glasson [7], in spite of the oxidizing atmosphere almost no sulfate formation occurs because of the low temperatures/. The induction time of 3.2 min between SO_2 admixture to the sample atmosphere and absorption /weight increase/ is very long for technical use. Treatment of dehydrated $Ca/OH/_2$ with a SO_2-containing atmosphere at 800° leads to about 68% conversion of the active CaO to sulfate. A strong dependence on the SO_2 concentration can be seen.

Binary systems are of enormous importance for the use of ceramic materials in many ranges /enamel technique, corrosion protection, space technology, etc./. By the use of thermoanalytical methods, combinable materials can be preselected with regard to the thermal expansion behaviour, and measurements of material stresses in binary systems are possible.

The lowest expansion differences can be detected in differential dilatometers /amplification 250/. The use of dilatometers for tension measurements on binary systems of dental ceramics has been described [8]. In a 3-point bending arrangement the tensions arising due to material differences and boundary-layer formations are measured or calculated from the bending of the sample. Tensions are linearly correlated to the bending. The maximum compressive stress for bimaterial systems for ceramic layers is 25 N/mm^2, which is far below the allowable stress of 150 N/mm^2 for dental ceramics.

Extreme applications of ceramic materials have become a routine field of TA practice by the adaptation or development of thermoanalytical instruments. This is applied, for example, in the fields of oxide ceramics and high-melting ceramics by the use of commercial units in the highest temperature range, up to 2400°.

CONCLUSION

High-temperature technology ceramics have traditionally offered an ideal field of application for thermoanalytical methods. New instrument systems and new fields of application for ceramic materials always involve actual problems for TA methods with a fluent change-over from research to routine control. The highly-developed instruments for TA make it possible to solve serious environmental problems and to obtain new knowledge on common materials and material systems.

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ZUSAMMENFASSUNG - Die Keramik ist traditionsgemäss ein Hauptanwendungsgebiet der thermoanalytischen Methoden. Veränderungen in der Technologie und in dem Umweltschutzproblemen geben neuen Anlass für die extensive Anwendung hochentwickelter TA-Geräte. Es wird gezeigt, dass die TA Schwierigkeiten im Produktionsprozess lösen kann, neue Informationen über den optimalen Gebrauch von Rohmaterialien liefert und weiters Anwendungsgebiete für die Keramik erschliesst.

Резюме - Керамика является традиционным объектом исследования методами термического анализа. Изменение технологии ее получения и возникшие при этом проблемы окружающей среды объясняют причины широкого использования хорошо разработанного в приборном отношении термического анализа. Показано, что ТА может разрешить трудности процесса получения керамики и дает новую информацию об оптимальном использования сырья для керамики.