

Possibilities of Thermal Analysis for the Evaluation of Construction Materials

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Abstract. The article deals with the use of thermal analysis as an effective tool for the evaluation of building materials. The applied method of combined DSC/TG analysis is briefly described. Its utilization is illustrated by analyzing a sample of carbonated concrete. The method has wide application in other sectors, including analysis techniques in forensic science.

Introduction

Various instrumental methods can be used for the analysis of building materials. Classical chemical analysis is not in high demand at present. Especially spectroscopic methods are applied. Information about chemical or phase composition of the material is obtained by using infrared techniques, X-ray spectroscopy or X-ray diffraction in short time. Phase composition knowledge is useful for certain materials, such as concrete or mortar materials. Complex mineral phases and their interactions with its surroundings are responsible for specific material properties. Highly accurate information about the phase composition is obtained by using X-ray diffraction, but phase quantitative analysis is more difficult. In this regard, thermal analysis seems to be highly competitive.

This method is based on the simple principle of monitoring the weight and temperature changes during heating of the sample. Analysis of the sample composition is possible through assessments of phase transformations. The disadvantage is reduced accuracy influenced by many factors. Especially each thermally reactive chemical mixture has a different temperature of conversion; the individual phases may thermally overlap. Previous standard measurements of chemical substances may be used as a comparative for this purpose. Nowadays there are also various libraries of thermal curves [8], and others can be found in a number of available scientific literatures [1]. At present, construction materials are relatively well understood with regard to thermal behavior and number of the phenomena has been well described. Thermal analysis can be conveniently used to obtain high-quality information about the composition and also about passed degradations for example due to carbonation for substances, such as concrete.

Thermal analysis

The thermal analysis term includes all methods, which study the properties of materials depending on heat treatment. The sample is thermally loaded with defined temperature ramps in the furnace and measuring instrument simultaneously records change in monitoring variables and temperature. Testing of clay minerals by heating curve method (differential thermal analysis without reference sample), which Le Chatelier published in 1887, is considered as the first application of thermal analysis[2].

Methods of thermal analysis. Methods of thermal analysis serve for phase composition determinations and are divided according to observed parameters of the material[3,4]:

- thermogravimetric analysis (TG), monitoring weight change of the sample;
- differential thermal analysis (DTA), evaluating temperature differences between test and reference sample;

- differential scanning calorimetry (DSC) monitoring heat flow that needs to be supplied into the system to maintain the same temperature of the test and reference sample.

Besides the phase composition of the material, changes in the mechanical, electrical, magnetic, or other properties can be examined in relation to operating temperature [3,4].

Modern instruments enable simultaneous measurement of several variables, thus information about different characteristics of the material is obtained. The typical examples are combinations of thermogravimetric and differential thermal analysis (TG / DTA), or thermogravimetric analysis and differential scanning calorimetry (TG / DSC) [4].

Results interpretation of thermal analysis. Several outputs can be considered as evaluation. Observation of exothermic and endothermic effects on the curve of heat flow is an essential element. The number of changes and their size can be determined in this way. Comparison with thermogravimetric curve is used to determine, whether the change is disruptive, such as a release of gases from compounds, or only structural, such as a changing the crystal structure [3].

Initial and final transformation temperature and its speed can be established at a more detailed analysis by using derivation curves. Derivation curves also allow distinguishing of overlapping effects in some cases. Measurement of weight changes is not difficult to perform with the determination of temperature limits; subsequently decomposition amount of the material can be calculated from these values for quantitative analysis. This analysis can also be done in dependence of the heat flow. Peak area of heat flow curves can be integrated, and thereby the amount of supplied or consumed heat is determined. For this analysis, it is necessary to operate with the thermodynamic processes during the phase transformation [3].

Laboratory of ICT – instrumentation

Analysis of the phase composition is determined by means of thermal analysis for different samples in the Laboratory of thermal properties, rheology and corrosion of building materials. For this purpose the instrument SDT Q600 from TA Instruments with simultaneous thermogravimetric analysis and differential scanning calorimetry (TG / DSC) is used [9].

Measurements of weight loss and changes in the heat flow can be performed up to the temperature 1500 ° C [6], which is reached in the sample vicinity with predetermined temperature profile. Burning atmosphere can also be selected depending to gas used [9]:

- oxidative - air;
- reductive - nitrogen (N₂).

This instrument is equipped with a horizontal balance with dual beam where a test and reference sample is placed into ceramic (up to 1500 ° C and volume of 90µL) or platinum cups (up to 1000 ° C and volume of 110µL) [9]. Direction of gas flow through the furnace of thermal analyzer is also horizontal, thus effectively removes decomposition products from the sample. [9]

Evaluation of building materials by thermal analysis

Evaluation of obtained DSC / TGA curves is relatively complicated. The outputs are processed by comparing graphic record with the curves database of known substances - standards. Weight changes and heat flowing relation to the ambient temperature are mainly observed in our case. The experience gained from previous measurements can significantly facilitate the evaluation of results.

Database of thermal analysis curves. The database of thermal analysis curves is an important tool for the identification of unknown materials. The final appearance of the graphic record is affected by heating rate. For this reason, the course of heating should be the same for the test and standard sample. The curves measured on samples of pure minerals are the most important for the processing of the results, because they serve both to identify monomineral substances, as well as resolution of the individual components of composite materials.

In this case, results in oxidizing and reducing atmospheres of the SDT Q600 are archived, for where the sample weight change (TGA) and the differential heat flow (DSC) is monitored in dependence

on the operating temperature[9]. The results can also be supplemented with the derivation of weight change (DTG) in dependence on temperature for the determination of the beginning and end of monitored processes. Heating rate is chosen $10^{\circ}\text{C} / \text{min}$ for all standards.

Stages of thermographic curves are possible to exemplify by decomposition of calcite (Fig. 1). Limestone (CaCO_3) starts to decompose at a temperature of 600°C to form calcium oxide (CaO) and carbon dioxide (CO_2). [2]

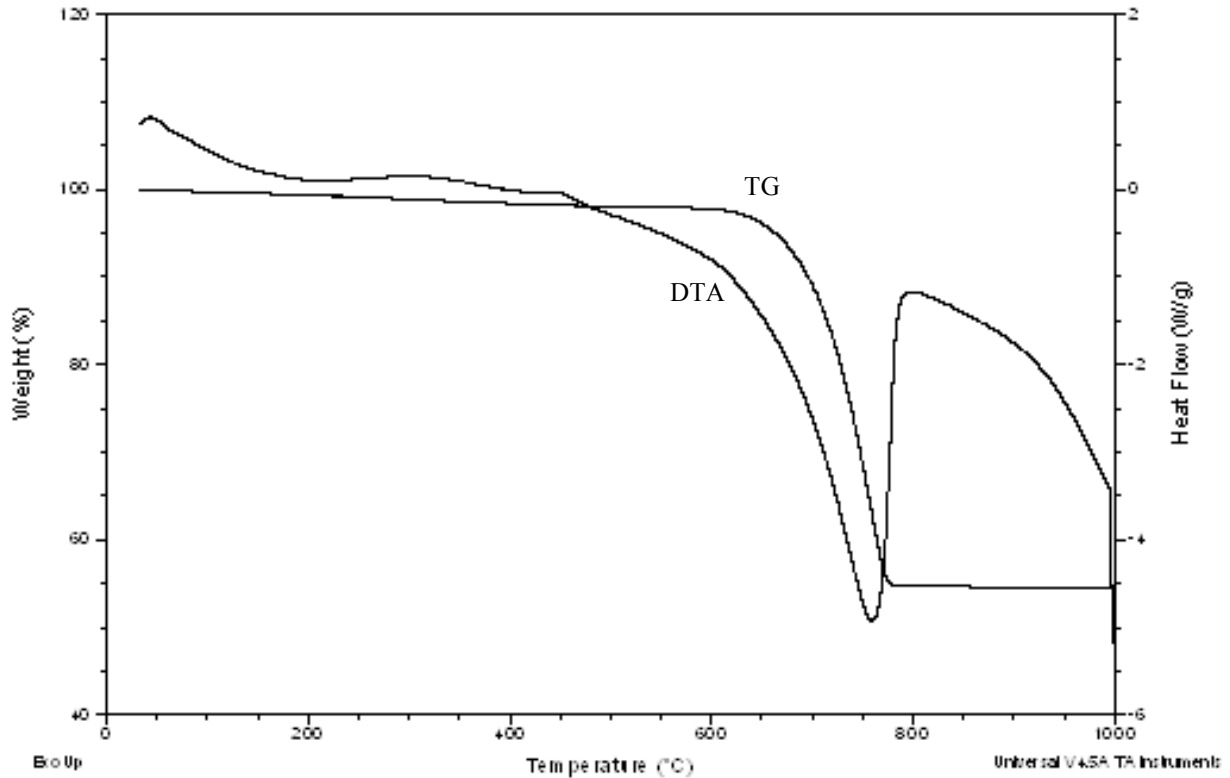


Fig. 1 Graphic record of CaCO_3 thermal analysis in oxidizing atmosphere

This phenomenon is called calcination and is used in the production of quicklime [2]. It is apparent at the heat flow record (Fig. 1) that this reaction is endothermic. Although this transformation is theoretically abrupt, in reality, it takes place a long period of time. This is caused by necessity to heat the whole analyzed sample at the required temperature. Specific surface areas of the sample and any chemical impurities in crystal structure, which contribute to the change of decomposition temperature, also have an impact.

Application of thermal analysis - determination of concrete carbonation. The principle of using the graphical curves can be well described in the example of concrete carbonation. Binders based on Portland cement are often used for the production of concrete, with them portlandite crystals ($\text{Ca}(\text{OH})_2$), and C-S-H gel with the alkaline nature form during a setting and hardening [7]. The material has a pH about 12, thereby reinforcement by steel bars is passivated and protected against corrosion [2,5,6,7]. The grains of portlandite ($\text{Ca}(\text{OH})_2$) react with carbon dioxide (CO_2) to form calcium carbonate (CaCO_3) during concrete carbonation [2,5,6,7].



This reaction proceeds very slowly from the surface to the depth due to the small amount of carbon dioxide contained in the air (0.03% - 0.1%) and depending on the ambient humidity [5]. Changing the pH of concretes is due to reducing the amount of portlandite accompanied by currently increasing concentration of calcium carbonate. Corrosion of steel reinforcement occurs at pH less than or equal to 9 [5,6,7]. Corrosion products have a larger volume than the original material, which

results in stress formation and delaminating of concrete covering layers (Fig. 2a). Corrosion is accelerated by removing the covering layer [5].



Fig. 2 Carbonation of concrete

a - delaminating of concrete covering layers and reinforcement corrosion, b - application of phenolphthalein

Application of phenolphthalein (Fig. 2b) as a pH indicator is a traditional method for determining the carbonation of concrete [5,6,7]:

- concrete without carbonation (with a pH greater than 9), will turn purple after spraying;
- concrete with carbonation (with a pH of less than 9) is colorless after application.

The carbonation depth is determined as the average width of the concrete, which is colorless after phenolphthalein application. However, products of carbonation are at a greater depth, where the pH is over the 9. In the case that the real depth with formation of CaCO_3 must be known, the analytical method must be applied [6]. For this purpose, thermal analysis was used. Powder sample of cement stone is thermally loaded in the oxidizing atmosphere with heat rate $10^\circ\text{C}/\text{min}$. to 1000°C , while the heat flow and the weight change is recorded. Several areas of the peaks, which occurs changes in the monitored variables (Table 1), can be distinguished on the graphic recording.

Tab. 1st Temperature range of mass loss of concrete with carbonation [6]

Temperature[$^\circ\text{C}$]	Cause of mass loss
about 100	Loss of free water
about 130	Loss of physically bound water
425 - 550	Dehydration $\text{Ca}(\text{OH})_2$
550 - 950	Decomposition of CaCO_3

Mass loss in two last points are to be deducted from the graphic record [5,6]:

- dehydration of portlandite: $\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$;
- decomposition of calcium carbonate: $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$.

The amount of residual calcium hydroxide and formed calcium carbonate in the sample can be determined from the values of mass loss and molar mass of each substance. In this way the dependence of carbonate amount can be expressed on the distance from the surface, and thus determine the actual depth of carbonation [6,7].

Figure (Fig. 3) shows comparison of the analysis of two concrete samples. One sample is without carbonatation and the other one is highly carbonated. Decomposition of calcium hydroxide is apparent in the area of $400 - 450^\circ\text{C}$ at non-carbonated sample. Small reaction is also in the 573°C , for which temperature modification of quartz crystal structure is responsible. Small decomposition reaction of CaCO_3 can also be seen, because a certain amount of calcite is also located in a concrete with good condition.

The difference between the thermal analysis curves of healthy and carbonated concrete (cement stone) is apparent from enclosed graph. Mass loss of calcium carbonate decomposition has a minimum value in concrete with a good condition (Fig. 3) and there is evident dehydration of portlandite. Carbonated concrete is characterized by a significant mass loss during calcinations of

CaCO_3 [6,7]. The absence of decomposition reaction of calcium hydroxide is obvious at first sight. Decomposition reaction of CaCO_3 is significantly growing. This reaction is more pronounced, because carbon dioxide is received during carbonation and carbonate has a much greater weight.

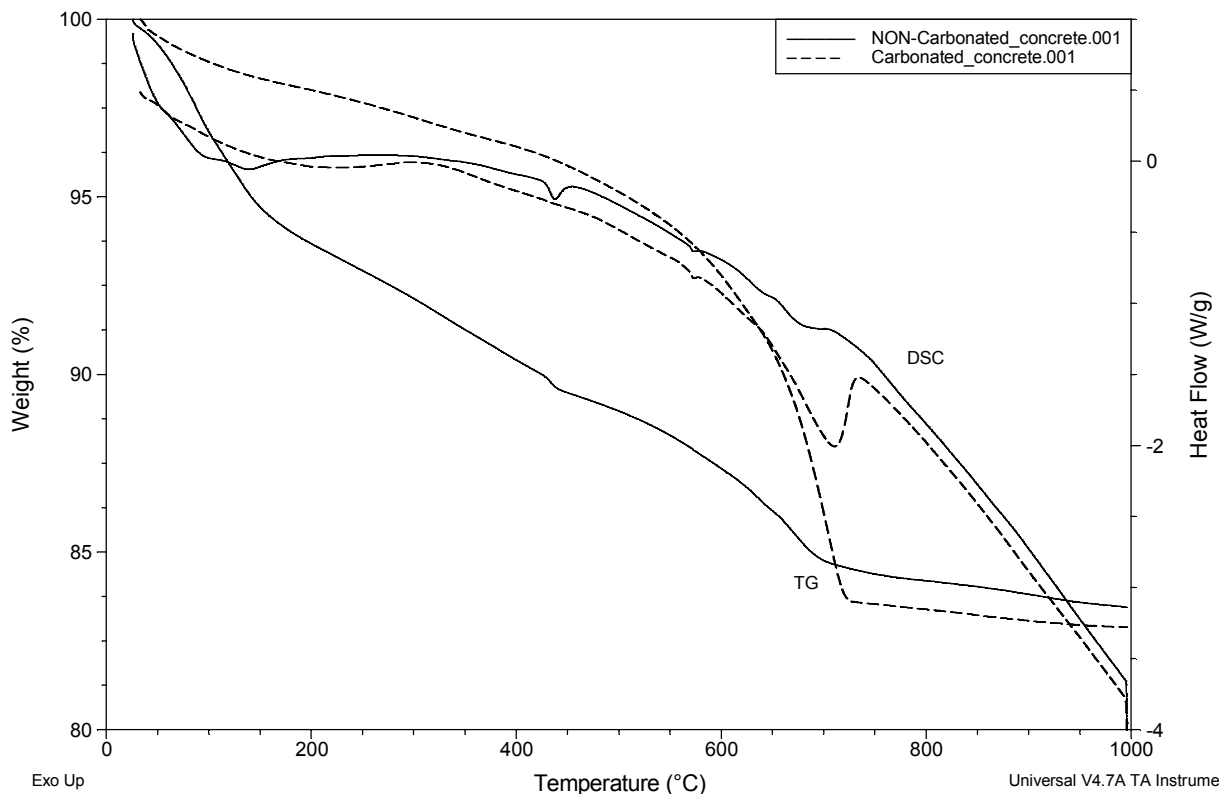


Fig. 3 Graphic record of thermal analysis of carbonated and non-carbonated concrete

Conclusion

Thermal analysis is advantageous due to its speed and accuracy for building materials purposes. Phase composition determining of different materials, mineral and organic origin, is possible generated on the basis of the TGA and DSC curves. In civil engineering, this method is used to analyze the stone, binders systems, ceramic materials, but also wood, plastics etc. Measurement accuracy is less than that of instrumental methods based on an interaction of electromagnetic radiation with the sample, but the combination of qualitative and quantitative measurement is advantageously at the evaluation of construction materials. The disadvantage is the necessity of a basic knowledge of the sample composition for the thermal reactions determination at least. Measurement by some other method is needed for determining of chemical and phase composition in the analysis of the unknown sample.

In the above text, the thermal analysis use was explained on the example of evaluation of concrete carbonation. At present, approximate indicator methods (e.g. application of phenolphthalein) are used primarily for this purpose, although they are not able to accurately determine the amount of CaCO_3 in the concrete and the real depth of carbonation. The use of TG/DSC analysis provides a relatively accurate description of the ongoing degradation, which can be effectively used in the assessment of structure and remediation design.

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References

- [1] V. S. Ramachandran, M. R. Paroli, J. J. Beaudoin, H. A. Delgado, Handbook of thermal analysis of construction materials, William Andrew, 2002.
- [2] L. Svoboda, a kol., Stavební hmoty, JAGA, Bratislava, 2008.
- [3] J. Šesták, Měření termofyzikálních vlastností pevných látek: teoretická termická analýza, Academia, Praha, 1982.
- [4] P. Štarha, Z. Trávníček, Termická analýza, UP Olomouc, Olomouc, 2011.
- [5] J. Witzany, a kol., PDR – Poruchy, degradace a rekonstrukce, ČVUT, Praha, 2010.
- [6] Ch. Chang – Feng, Ch. Jing - Wen, The experimental investigation of concrete carbonation depth, Cement and Concrete Research 36 (2006) 1760-1767.
- [7] M. Thiery, G. Villain, P. Dangla, G. Platret, Investigation of the carbonation front shape on cementitious materials: Effects of the chemical kinetics, Cement and Concrete Research 37 (2007) 1047-1058.
- [8] Atlas of Thermoanalytical Curves: (TG-, DTG-, DTA-curves Measured Simultaneously). Hayden and Son, 1977.
- [9] TA Instruments, url: <http://www.tainstruments.com>