Application of thermogravimetric analysis for characterization of clay as supplementary cementitious material

Matea Flegar[1], Asst. Prof. Marijana Serdar[2], Diana Londono-Zuluaga[3], PhD, Prof. Karen Scrivener[4]

[1]University of Zagreb, Faculty of Civil Engineering, Department of Materials, matea.flegar@grad.unizg.hr
[2]University of Zagreb, Faculty of Civil Engineering, Department of Materials, marijana.serdar@grad.unizg.hr
[3]Laboratory of Construction Materials, École Polytechnique Fédérale de Lausanne, diana.londonozuluaga@epfl.ch
[4]Laboratory of Construction Materials, École Polytechnique Fédérale de Lausanne, karen.scrivener@epfl.ch

Abstract

High-volume cement replacements can potentially reduce carbon dioxide emissions caused by cement production. Current research aims to find the most optimum locally available materials that can serve as replacement for cement. Thermogravimetric analysis (TGA) ranks among the methods used to characterize potential materials. This paper presents results of such analysis performed on six clay soil samples. The approximated quantity of clay mineral, calculated by means of TGA, is compared with the reactivity test (R3 test) using isothermal calorimetry. The results indicate that selected soil samples can be considered as low-grade kaolinitic clays. Nevertheless, they show a good correlation between clay mineral content and reactivity of the sample.

Key words: Thermogravimetric analysis, cementitious materials, clay, kaolin content, R3 test

Upotreba termogravimetrijske analize kod karakterizacije glina kao cementnih dodataka

Sažetak

Korištenje velikih udjela cementnih dodataka može utjecati na smanjenje emisija ugljikovog dioksida uzrokovanih proizvodnjom cementa. Istraživanja su usmjerena prema pronalasku najoptimalnijih lokalno dostupnih materijala koji mogu poslužiti kao cementni dodaci. Termogravimetrijska analiza (TGA) jedna je od metoda koja se koristi za karakterizaciju potencijalnih materijala. U radu su prikazani rezultati takve analize provedeni na šest uzoraka glina. Aproksimirana količina minerala kaolinita dobivena TGA-om uspoređena je s količinom oslobođene topline prilikom ispitivanja reaktivnosti uz pomoć izotermalne kalorimetrije (R3 metodom). Rezultati ukazuju na ovisnost reaktivnosti gline o sadržaju tog minerala, te na smanjeni udio kaolina u ispitanim materijalima u odnosu na gline iz literature.

Ključne riječi: termogravimetrijska analiza, cementni dodatci, gline, sadržaj kaolina, R3 test

1 Introduction to the use of thermogravimetric analysis

Faced with the growing need to reduce the CO_2 intensive cement clinker, researchers are constantly investigating new materials that can be used as cement replacements. The quest for new cementitious materials, that could satisfy current mechanical and durability requirements when used for concrete, pointed to the need for advanced characterisation techniques. These approaches rely on the knowledge of material structure, chemical and mineralogical composition, and physical properties of particles. Current research aims to correlate various characterising parameters to rank possible supplementary cementitious materials (SCMs) [1-2]. Thermogravimetric analysis (TGA) is one of advanced techniques used in such research. Thermogravimetry (TG) is a widely spread technique that measures and tracks mass change as a function of temperature. In the field of cement science, it is used for quantification and identification of minerals and hydrates. It is a powerful tool that can also detect amorphous phases, such as C-S-H or AH_3, which is why it is often used as a technique complementary to X-ray diffraction (XRD).

1.1 Parameters that influence thermogravimetric measurement

The results of thermogravimetric analysis are subject to various influences such as device settings, sample preparation and/or material composition. The device settings that affect the measurement are: heating rate, gas flow rate, type of thermocouples, vessel shape, and sample particle arrangement [3]. The preparation of samples is equally important and can also have a major impact. Some of the factors that can influence the results include sampling, particle size of material, sample amount, hydration stoppage and drying method [3–6]. It is emphasized in every study that a constant procedure is of highest significance for ensuring reliable and repeatable results. Salvador et al. [6] focused their analysis on the influence of grinding process and gas flow rate, while Scrivener et al. [4] pointed out that the material sample should not be pressed into the measuring vessel but should rather be placed lightly and evenly. Although it is a common practice to normalize TGA and DTA data by weight (100% by weight), which facilitates comparison of different sample masses, it has been shown that larger differences in sample mass give unreliable results [4]. Scrivener et al [4] also recommend that the value of 50 mg be adopted as an optimum sample mass for TGA, while Smykatz-Kloss [5] lists other recommendations as shown in Table 1.

Table 1. Device setup and sample preparation recommendations for thermogravimetric analysis [5]

Parameter	Recommendation	
Particle size	Clay: 0.6 - 2 μm Ø	
	Other material: 60 - 200 Ø	
Oven	Uniform air flow	
Heating rate	10 °C/min	
Sampling	sample lightly placed (not pressed) in the vessel	
Sample hardness	Mohs scale	Grinding method
Extremely hard sample	> 6,5	3-minute manual crushing with a mortar
Hard sample	4,5 – 6,5	1-minute grinding in a ball mill at low speed (500 g, 3 balls < 2,5 cm Ø)
Soft sample	< 4,5	2-minute manual pulverization with a grinder

1.2 Qualification and quantification of most common phases

Minerals and hydrates undergo several decomposing reactions when heated: dehydration, dehydroxylation, decarbonation, oxidation, phase change, or melting [4]. These reactions are usually associated with the change in mass and/or heat release, and they occur in a specific temperature range. This knowledge provides information for identification or even quantification of certain phases. The data obtained from TGA are displayed either as weight loss vs. temperature or as a first derivative of that curve (Figure 1). The derivative curve (DTG) emphasizes the temperature ranges of significant mass loss.
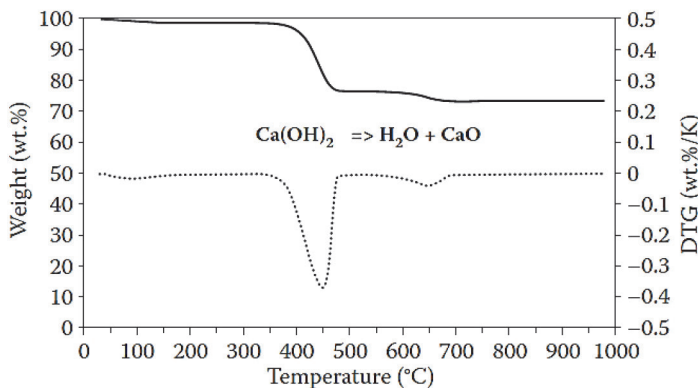

Figure 1. Mass loss recorded by TGA (solid line) and first derivative of that curve - DTG (dashed line) [4]

As mentioned before, TGA is often used to characterise cementitious materials such as limestone, fly ash, slag and clay. The analysis is based on distinctive DTG curve peeks that can be observed when analysing these materials. Natural pozzolans (and

other materials) that are collected from open landfills most often contain some moisture. This is why a significant DTG peak and a higher mass drop at lower temperatures (up to 200° C) can be observed, which is related to the loss of free and chemically-bound water [7]. Calcium rich materials, such as fly ash or some slags, can contain portlandite [$Ca(OH)_2$], which dehydroxylates [$Ca(OH)_2 \rightarrow CaO + H_2O$] in the temperature range of approximately 460 °C [4]. Dehydroxylation of clay minerals starts at around 350 °C and ends near 850 °C (depending on the mineralogy) when clay structure collapses and forms amorphous phases [8]. This is a desirable process that activates clay minerals, and they obtain pozzolanic properties. The most reactive clay mineral is kaolinite, which transforms its structure between 450 °C and 550 °C forming metakaolin [9], but often overlaps with the dehydroxylation of illite. Ground limestone is a common cementitious material, lately often used in ternary cement blends [10]. Calcium carbonate ($CaCO_3$) is the main element of limestone but can also be found in other cementitious materials. The $CaCO_3$ content can be determined by measuring the mass loss between 700 °C to 850 °C, which is the mass of carbon dioxide loss due to decomposition of $CaCO_3$ [11]. The weight loss caused by decomposition of these elements can be used for their quantification using molecular masses.

2 Thermogravimetric analysis of local clay samples

2.1 Materials and methods

Six samples of clay soil were selected and analysed as a part of the ACT project. These materials, natural clays originating from the Southeast Europe, were collected from five different excavation sites. All samples were treated prior to the measurement by drying for 24±2 h at 60±5 °C in an aerated oven and by grinding in a disc mill for 30 seconds.

Chemical analysis and particle size of treated samples were determined by X-ray fluorescence (XRF) and particle-size distribution (PSD), respectively. The corresponding test results are shown in Table 2 with respect to the ordinary Portland cement (OPC) sample. All clays show a higher amount of silica (SiO_2) and a significantly smaller amount of calcium oxide (CaO) when compared to the CEM I 42,5 R sample (OPC). The difference is also visible in alkali content, where clays exhibit a higher sum of sodium (Na_2O) and potassium oxides (K_2O). An average particle size of all clays varies from 8.2 to 15.4 µm, which is similar to the OPC average particle size of 9.95 µm.

Table 2. Chemical composition and particle size of clay samples after treatment

Label	Chemical composition (%)											Average particle size
	CaO	SiO₂	Al₂O₃	Fe₂O₃	MgO	P₂O₅	Na₂O	K₂O	TiO₂	MnO	SO₃	D (v, 0.5)
OPC	64.04	19.32	4.86	2.94	1.83	0	0.23	0.82	0	0	2.75	9.95
TOP	2.09	64.59	20.55	6.39	1.74	0.34	0.94	2.32	0.89	0.09	0.10	10
KaVa_1	2.01	63.06	24.97	3.09	1.38	0.28	0.48	3.95	0.71	0.01	0.07	8.6
KaVa_2	2.02	63.79	24.26	3.42	1.28	0.28	0.50	3.75	0.64	0.01	0.08	8.2
NC	2.57	63.70	19.53	6.80	2.34	0.35	1.26	2.52	0.76	0.08	0.12	13.4
SlVk	2.53	63.87	19.28	6.55	2.25	0.43	1.27	2.91	0.77	0.10	0.08	14.1
IGM	2.43	64.28	19.75	6.26	2.11	0.39	1.30	2.54	0.80	0.09	0.07	15.4

The thermogravimetric analysis was performed in the Laboratory for advanced testing of materials (LATOM) at the Faculty of Civil Engineering, University of Zagreb. For each TGA measurement, 50±5 mg of material were placed in a platinum crucible. When transferred to the instrument, the samples were first stabilised at 30 °C, then heated until 800 °C at a constant heating rate of 20 °C/min, and at a constant nitrogen gas flow rate of 30 ml/min. Lastly, the mass loss was calculated by means of the stepwise tangential method using Trios software [12] within predefined temperature ranges. The clay mineral content was approximated according the stated formula, where the mass loss in the range of dehydroxylation was multiplied with the fraction of molecular masses:

$$Clay_{content} = WL_{dehydroxylation} \cdot \frac{m_{clay\,min}}{n \cdot m_{H_2O}}$$
(1)

For the purpose of preliminary characterisation, an assumption was made that the mass loss between 350 °C and 600 °C is connected to the dehydroxylation of kaolinite ($WL_{dehydroxylation}$). For a simplified calculation of kaolinite content this value was multiplied with the fraction of kaolinite molecular mass ($m_{kaolinite}$=256 g/mol) and two molecules of water (m_{water}=18 g/mol) [13].

The approximated kaolinite content was then correlated to the results obtained from the R3 test. This test was developed for the RILEM TC-267 committee to address the reactivity of SCMs such as clays. It is performed on pastes using isothermal calorimetry set at 40 °C to enhance the reaction. The pastes are made from blends containing 10 g of SCM and the mix of solids with the ratio of Ca(OH)₂/SCM and CaCO₃/SCM of 3 and ½, respectively. The solution used in the paste is made of alkalis, KOH and K₂SO₄. All reagents were held for 24h at a constant temperature of

40 °C prior the mixing. The mixing was conducted using a high shear mixer at 1600 ± 50 rpm for 2 min after which 15 g of pastes were immediately placed into the glass vial and into the calorimeter.

2.2   Results

TGA results are shown in Figure 2 which displays the weight loss curve as well as the DTG curve for each of the six clay samples. The first weight loss can be observed due to dehydration of water and moisture content in clays, marked as free water. This indicates that the drying procedure was not completed and should be prolonged or performed at a higher temperature. The biggest DTG peak appears from 350 °C to 600 °C in all clays. This is the characteristic dehydroxylation temperature of most common clay minerals – kaolinite and illite, which partially overlap. The various clay minerals present have different reactivities: namely, highly reactive kaolinite (1:1) clay versus much lower reactivity of the 2:1 clays. The difference between clay samples is most evident in this temperature range, where samples KaVa_1 followed by KaVa_2 show the biggest DTG peek.
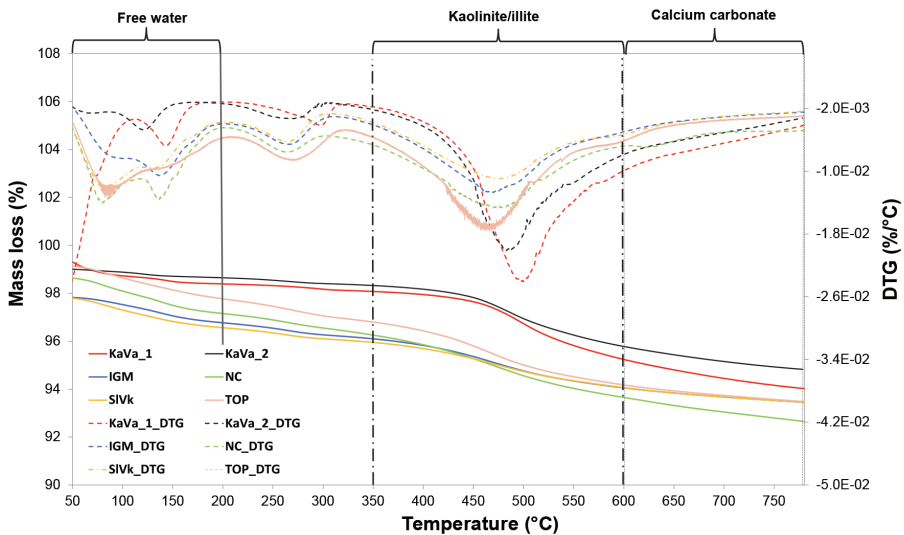

Figure 2. Thermogravimetric analysis of selected clay samples showing mass loss (solid line) and derivative curve (dashed line)

Table 2 shows obtained mass loss percentage in the distinctive temperature range, from 350°C to 600°C. The mass loss obtained from the TG analysis was used to calculate the clay mineral content. Sample KaVa_1 has the highest value of clay minerals, more than 21%. KaVa_2 is the second ranked sample with 19.29%, followed by TOP and NC samples. Samples SlVk and IGM have the lowest quantity of clay minerals, less than 12% of the total mass.

Table 3. Mass loss obtained by thermogravimetric analysis and calculated clay mineral content

Sample	Mass loss [%] 350 – 600	Approximated kaolinite content [%]
KaVa_1	2.99	21.26
KaVa_2	2.713	19.29
IGM	1.616	11.49
NC	2.326	16.54
SlVk	1.656	11.78
TOP	2.69	19.13

The outputs of R3 test are shown in Figure 3 where cumulative heat release reported per g of SCM in time is shown. All clay samples display a similar trend, fast heat release in the first 15 h of reaction, and then a slower reaction after 24h. Sample KaVa_1 again shows the highest value, followed by KaVa_2, Top, and NC samples. The lowest heat release is exhibited by IGM and SlVk samples.
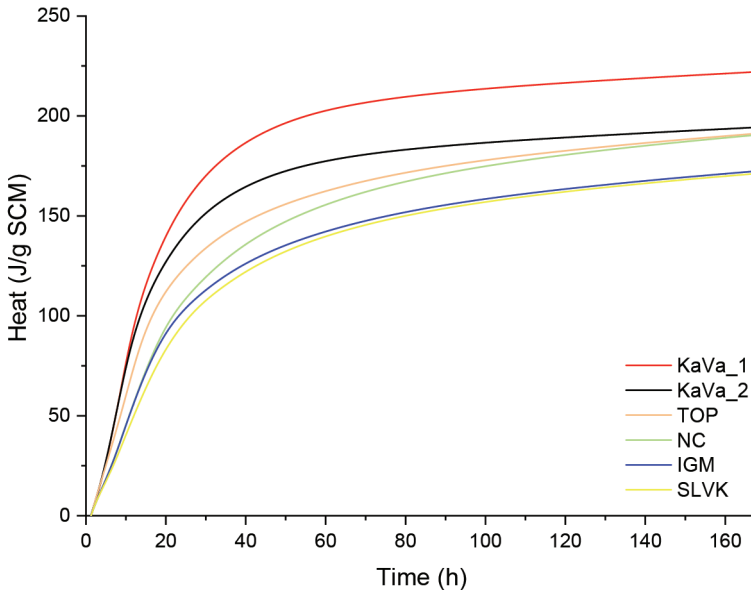
Figure 3. R3 test results shown as heat release in time

The correlation of results obtained by the two tests, the TGA test and R3 test, is shown in Figure 4. The correlation coefficient (R^2) indicates a strong positive linear relationship between the results, which implies the influence of clay mineral content on the reactivity of clay as SCM.
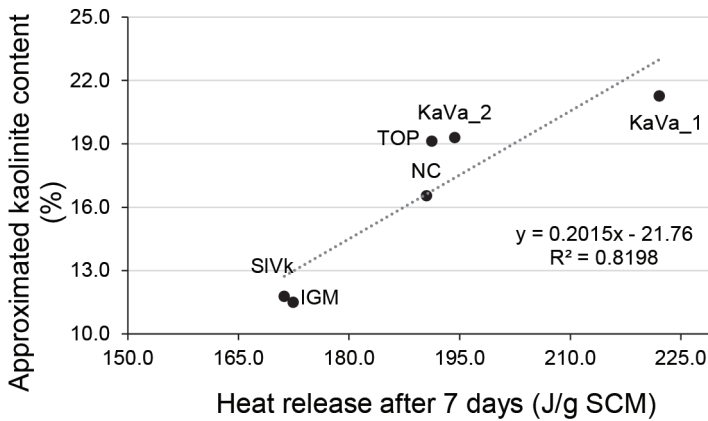
Figure 4. Correlation of clay mineral content and heat release after 7 days for each clay sample

3 Conclusion and further research

This paper presents an example of thermogravimetric analysis of supplementary cementitious materials focusing on characterisation of raw clay. All selected samples show a substantial weight loss in a temperature range from 350 °C to 800 °C, which is typical for the dehydroxylation process of clay minerals. This process causes the distinctive clay minerals to convert into an amorphous state. What should be considered is that the DTG curves of several clay minerals overlap in this temperature range, which makes it difficult to differentiate them. The difference could be more visible in the DTG curve by performing a more precise measurement in the critical temperature range (using lover heating rate). The presence of minerals kaolinite, illite and montmorillonite should be confirmed with other methods such as XRD. The mass fractions of all relevant clay minerals could then be calculated and compared using idealised stoichiometries. Nevertheless, with a simplified calculation and assumption that the weight loss from 350 °C to 600 °C is related to the dehydroxylation of kaolinite, we could calculate and rank the selected clays accordingly. The clay sample KaVa_1 has the highest value, with 21%, while the IGM sample has the lowest value of only 11%. These results indicate that selected samples can be considered as low-grade kaolinitic clays and should be subjected to higher calcination temperatures than the kaolinitic ones [14 - 15] when used as SCMs. The influence of clay mineral content on the increase of pozzolanic properties of clays was verified by correlation to the R3 test results. The outputs again show sample KaVa_1 as the most suitable one, while the lowest reactivity is exhibited by SlVk and IGM samples.

Further research should be focused on a precise assessment of all clay minerals, followed by activation of the most viable samples. This is a part of the ACT project that aims to optimise cement substitution for standard strength concrete. In the upcoming period the chemical and physical characteristics of local materials, obtained by advanced testing methods, will be correlated with mechanical properties of mortars containing these SCMs. This will provide an insight into the most important parameters of raw materials that could potentially serve as high volume cement replacements.

Acknowledgement

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