

Investigation of the segregation behavior of different mortar constituents with TGA/SDTA

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Introduction

The mineral constituents of mortar mixtures can be divided into two main groups - “reactive binders” and “inert fillers”. By mineral binders, we usually mean cement, e.g. Portland cement or aluminous (high-alumina) cement, anhydrite and/or hemihydrate (calcium sulfate) that hydrate when mixed with water. The hydrates form a solid matrix that binds the mortar together. Quartz or carbonate-rich sand and/or their finely crushed powder are used as fillers. Other possible mortar constituents are latent hydraulic binders, glasses, lightweight fillers and a large number of organic additives such as cellulose ethers and redispersible powders.

Fresh mortar is made by adding water and mixing well. The particular working consistency of the mortar depends on the application. When used as an adhesive for wall tiles, the shear strength and viscosity should be on the high side. For self-leveling flooring, the mass may segregate to certain degree. The mortar must remain homogeneous, i.e. the coarse mineral constituents should not settle, and the water with the dissolved and dispersed fine components should not rise to the surface too much.

This article describes how the segregation behavior of freshly made mortar was quantitatively analyzed using TGA/SDTA. A simple tile adhesive recipe was used as an example.

Sample preparation

The tile adhesive consists of 40% Portland cement (CEM I 52.5 R, JCF, Wildegg), 59.6% quartz sand (0.1-0.3 mm, Zimmerli Mineralwerke, Zürich) and 0.4% methylhydroxyethyl cellulose (MHEC 15000 PFF from Aqualon). 100 g of the dry mixture were stirred with 23 g of water and transferred to a concrete slab with a suitable tool. After five minutes, a 50x50 mm earthenware tile was placed on the mortar and a load of 2 kg applied. This compressed the mortar layer to 1.6 mm.

After setting, the tile was broken off and samples of the mortar were taken sequentially along a vertical profile from the tile surface to the concrete slab. The weight of each sample compared with the total weight of all the samples allowed the distance along the 1.6 mm long profile to be approximately estimated.

Measurements with the TGA/SDTA851^e

The TGA curves show three significant weight loss steps. The first at about 100 °C has to do with the drying (capillary pore residual water) and/or with the dehydration of ettringite. The first step is not evaluated here because of the uncertainty in the interpretation. The second step at about 450 °C is due to the dehydration of $\text{Ca}(\text{OH})_2$ (portlandite). Notice the reduced portlandite content in the recipe containing MHEC. This indicates a reduced degree of hydration, probably in connection with the effect of the cellulose ether, which retards setting. The third weight loss step at about 700 °C can be attributed to the decarbonation of CaCO_3 . The carbonate is

however not present in the original mixture and must therefore arise from a carbonisation reaction. This interpretation is supported by the fact that the carbonate content correlates with the portlandite content and has a tendency to increase toward the concrete slab.

The SDTA curves show that the three weight loss steps each correspond to endothermic processes. In addition there is an exothermic process at about 260 °C and another endothermic process at about 570 °C. These two peaks correspond to the strongly exothermic decomposition of MHEC and the solid-solid transition of quartz. The MHEC and quartz content can therefore be quantitatively determined by evaluating the SDTA signal. The decomposition of MHEC in fact also causes a weight loss. However, with low MHEC concentrations (in this case 0.4%), this weight loss step is completely hidden by the drying and dehydration processes of the ettringite. In this case, only the quantitative evaluation of the exothermic SDTA peak allows reliable information on the MHEC content

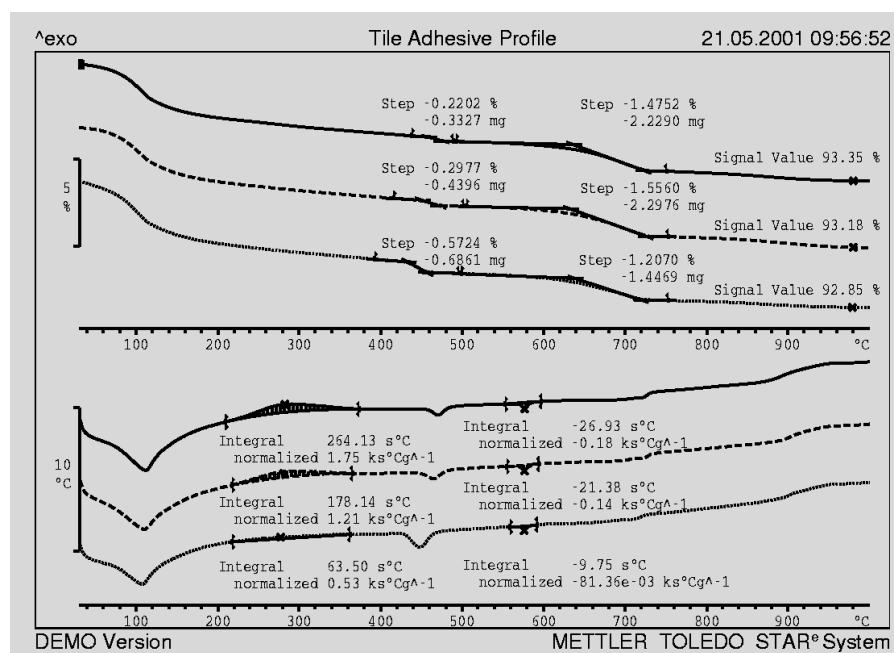


Fig. 1. The TGA and SDTA curves of three samples. The dotted curve shows the results of a TGA analysis of a reference mortar sample consisting of Portland cement and quartz sand that did not contain any MHEC. The uppermost sample in contact with the tile (continuous line) and the sample in the middle of the mortar bed (dashed line) are shown as examples of the 5 individual samples.

to be obtained. To do this, it is of course necessary to measure samples containing different known amounts of MHEC and to construct a calibration curve. A similar calibration curve allows the weak endothermic α - to β -quartz transition at 573 °C to be used for quantitative purposes.

Quantification of the MHEC and quartz content using calibration curves

To obtain the necessary calibration curves, samples containing different known amounts of constituents in question have to be analyzed beforehand. As an example, Figure 2 shows the SDTA curves of 6 samples containing different percentages of quartz.

A plot of the quartz content as a function of the SDTA peak area normalized to the sample weight yields the calibration function shown in Figure 3 needed for the determination of the quartz content from SDTA data. Frequently, in the first heating measurement, organic residues also oxidize whose combustion enthalpy is many times larger than the approximately 8 J/g liberated in the solid-solid quartz transition. Even quartz contents over 50% are then difficult to determine with the SDTA peak area of the α - to β -quartz transition. Each sample should therefore be measured a second time at the same heating rate used to obtain the quartz calibration curve. In the example described here, each sample was first measured from 30 °C to

1000 °C at 10 K/min in air (50 ml/min). For the quartz determination, the residue from the first measurement was cooled and then measured again from 500 °C to 620 °C at 10 K/min under N₂ (50 ml/min). It is important to note that each type of quartz leads to a different, but in each case very reproducible, calibration curve. For this reason, a calibration curve obtained with one type of quartz should never be used to quantify a different type of quartz.

Figure 4 shows the calibration curve for mortar with different MHEC contents. The calibration curve was obtained in the same way as that for the quartz content. Both calibration curves show correlation coefficients of 0.99.

The segregation behavior of individual mortar constituents

If the contents of MHEC, portlandite, calcium carbonate, quartz sand and Portland cement evaluated from the 5 TGA/SDTA measurement curves are plotted as a function of the position of the sample along the vertical section through the 1.6 mm thick sample of tile adhesive, the relationships shown in Figures 5, 6 and 7 are obtained.

The distribution curve for MHEC (Fig. 5) shows a clear enrichment effect towards the tile and the concrete slab. In principle, there are several fractionating mechanisms: the surface activity of MHEC could

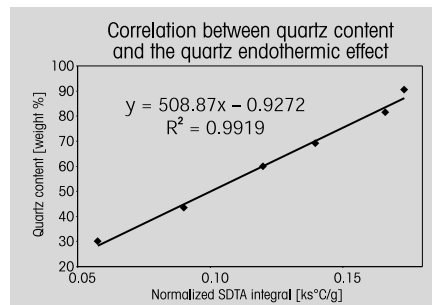


Fig. 3. Calibration curve for the determination of the quartz content using SDTA peak areas

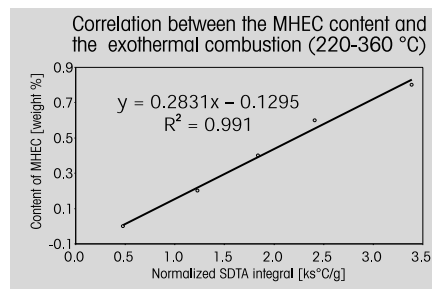


Fig. 4. Calibration curve for the determination of the MHEC content from SDTA measurements

cause enrichment on the surface of the mortar even before laying the tile. On the other hand, MHEC is dissolved in mortar water and migrates with the pore water at the evaporation front (mortar surface before laying the tile) or towards a porous tile and the concrete slab, both of which are highly porous materials that absorb well.

The concentrations of quartz sand and Portland cement show a variation that is complimentary within a range of about 6 wt %. No clear enrichment effect is noticeable (Figure 6). The viscosity of the fresh mortar apparently prevents sedimentation of the quartz sand. Since the ignition residues of all the samples vary within a small range of 92.7 to 93.6 wt %, an enrichment of quartz sand has a direct effect on the concentration of the second main constituent, the cement.

The distribution profiles for Ca(OH)₂ and CaCO₃ (Fig. 7) show a slight increase of the content of both phases toward the concrete slab. Ca(OH)₂ and CaCO₃ enrichment can on the one hand result from primary cement enrichment and on the other hand from a different degree of hydration and carbonate formation. An additional complication in the interpretation is that carbonate formation occurs at the expense of Ca(OH)₂, but this does not occur everywhere to the same extent. In general, how-

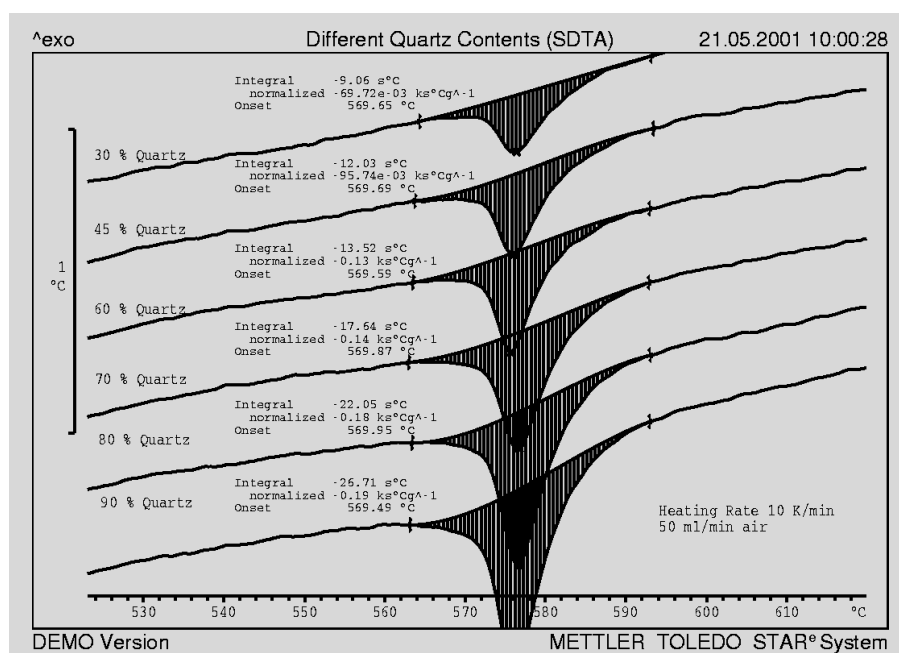


Fig. 2. SDTA curves of six different dry mixtures with known quartz/cement ratios. The peaks are integrated over the same temperature range.

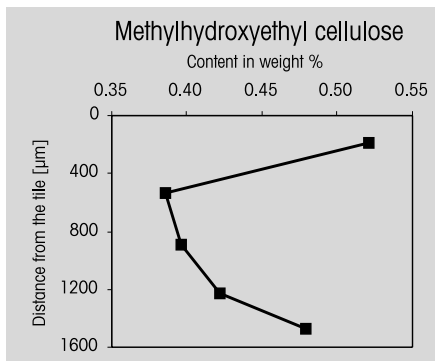


Fig. 5. Depth profile for MHEC in a tile adhesive

ever, one notices a parallel relationship between the concentrations of $\text{Ca}(\text{OH})_2$ and CaCO_3 , which means that hydration and carbonate formation accompany one another. The fact that the distribution

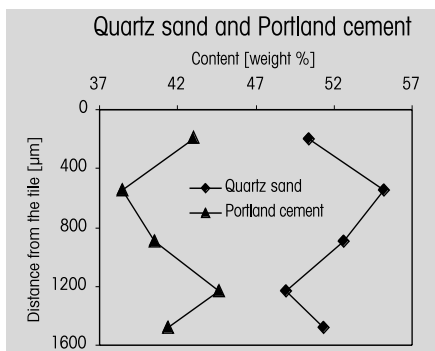


Fig. 6. Depth profile for the quartz and Portland cement content in a tile adhesive

curves of $\text{Ca}(\text{OH})_2$ and CaCO_3 do not exactly follow the cement distribution is evidence for the presence of different local degrees of hydration.

The concentrations by weight of the different constituents of the mortar in the original mixture can be determined by averaging the concentrations of the different mortar constituents along the depth profile. The ratio of the sample weight to the total weight of all the samples is used as the weight factor for the calculation of the mean value for each sample. On the basis of the TGA/SDTA measurements described here, one finds values of 0.44% MHEC, 41.5% cement and 51.7% quartz sand for the composition of the original mortar

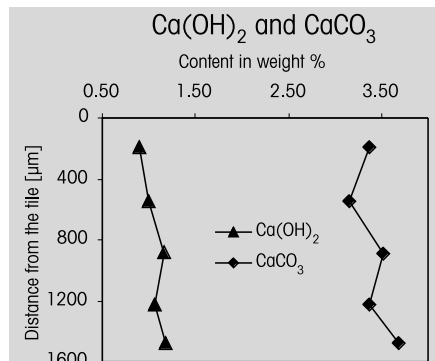


Fig. 7. Depth profiles for Portlandite and calcium carbonate in a tile adhesive

mixture. The rest is free pore water and bound H_2O and CO_2 from the various hydrates and carbonates. Corresponding to the known composition of the dry mixture, the mortar after setting should contain 0.38% MHEC, 38% cement and 56% quartz sand. The comparison with the values determined from the TGA/SDTA measurements shows a relative deviation of 16% in the case of MHEC and deviations of about 10% for the cement and quartz contents. Taking the low content of MHEC into account, the results can be regarded as being sufficiently accurate.

Summary and conclusions

To investigate the segregation behavior in the fresh mortar state, several samples were taken along a depth profile of the mortar after setting. The composition of the samples was determined quantitatively using TGA/SDTA, which allowed the heterogeneous distribution curve of each mortar constituent to be determined over the entire length of the profile. Hydrates (e.g. portlandite) and carbonates can be stoichiometrically quantified via each weight loss step of their dehydration/carbonate decomposition. In principle organic additives such as methylhydroxyethyl cellulose (MHEC) can also be quantified via the weight loss step of their exothermal combustion reaction. The relative amounts of organic additives are frequently so small that the corresponding weight loss steps are overlaid by

dehydration reactions of different hydrates (C-S-H phases?). In the case described, however, the relatively strong exothermic decomposition of the small amount of 0.4% MHEC produces a clear SDTA signal. Using a calibration curve set up beforehand, the MHEC content can be determined with sufficient accuracy even for low MHEC contents using the SDTA peak area.

Quartz fillers and cements are thermally stable in the temperature range of the measurements and together make up the ignition residue. The quartz content can also be quantified using the endothermic transition from α - to β -quartz at 573 °C by means of a calibration curve. The cement content is obtained from the difference between the ignition residue and the quartz content.

In addition the inhomogeneous distribution of substances such as the enrichment of MHEC toward the tile and concrete slab can be clearly shown using the depth profiles for different mortar constituents obtained from TGA/SDTA measurements. All in all one can say that TGA/SDTA is a very good method for the analysis of mortar. If the mortar systems are not too complex, all the important constituents can be quantitatively or semi-quantitatively determined. In addition the inhomogeneous enrichment of substances can be detected, which in turn yields information on different fractionization processes in the fresh mortar state (sedimentation, surface activity and migration with the pore water) and also after setting (different local degrees of hydration and carbonate formation).

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