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Hydration of a Portland cement blended with calcium carbonate

Jo Dweck[a,*], Pedro Mauricio Buchler[b],
Antonio Carlos Vieira Coelho[b], Frank K. Cartledge[c]

[a]*Inorganic Process Department, School of Chemistry, Federal University of Rio de Janeiro,
Bloco E do CT, Sala E-206, Cidade Universitária, 21900 Rio de Janeiro, Brazil*
[b]*Chemical Engineering Department, Polithecnic School, University of São Paulo, São Paulo, Brazil*
[c]*Chemistry Department, Louisiana State University, Baton Rouge, LA 70803, USA*

Abstract

The hydration of a commercial Portland cement blended with calcium carbonate was studied by thermal analysis. TG, DTA and DTG analyses were performed on pastes prepared with a water to cement weight ratio of 0.5, after different setting times during the first 28 days of hydration. The analyses were run from 28°C to 1000°C with a 10°C/min heating rate and 100 ml/min of air as the purge gas. All the analyses were performed after a drying step at 28°C in the equipment itself, using the purge gas as the drying agent, resulting in a more effective and less time-consuming method than other conventional drying procedures.

The original cement contains a partially decomposed dihydrated calcium sulfate, which is regenerated after 1 h of hydration and is consumed in about 16 h of setting. The results indicate that TG and DTG curves are faster and more precise tools than DTA curves to identify and to quantify all the main hydrated and carbonated phases which are present in the pastes, especially in the case of this cement blended with calcium carbonate, the total content of which cannot be estimated correctly by DTA as hydration proceeds. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The solidification/stabilization of hazardous wastes by cement-based binders is a technology which has been applied to many types of wastes and industrial effluents, mainly those containing heavy metals. The process has the potential for effectively immobilizing hazardous constituents, but may not do so if the cement matrix is altered by the waste. Consequently, we are interested in developing convenient and accurate tools for determining the composition of cement pastes. The present paper presents a study, by thermal analysis, of the hydration of a Portland cement blended with calcium carbonate, which is being used by the authors to solidify tanning wastes. The data are being used as a reference to compare the changes in the cement

* Corresponding author. Tel.: +55-21-590-3192; fax: +55-21-590-4991.
E-mail address: dweck@h2o.eq.ufj.br (J. Dweck).

hydration during the solidification caused by the presence of the waste itself or by immobilizing additives which are being used.

Until the 1970s the thermoanalytical characterization of cements and the study of their hydration has been mainly done by differential thermal analysis (DTA) [1,2]. Since then thermogravimetry (TG), semi-isothermal thermogravimetry, derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) have also been used [3–6].

Cement hydration is a process which occurs slowly, and measures of mechanical performance are typically carried out after 28 days of cure. However, solidification is observed during the first day of cure, and knowledge of the kinetics of the cement hydration from its beginning is a key factor for better understanding the process. Thus, in this work, TG, DTA and DTG analyses were performed on pastes prepared with a water-to-cement weight ratio (w/c) of 0.5, after different hydration times during a 28 day period. To avoid interference by the non reacted residual water, all the analyses were performed after a drying step at $28°C$ performed in the equipment itself, using air as the drying agent, resulting in a more effective and less time-consuming method than other conventional drying procedures [1].

Portland cements contain gypsum that is added to the clinker to prevent flash set by the aluminate fraction. During the milling process, the calcium sulfate, which is originally the dihydrate, may be partially decomposed through water loss. In addition, this cement clinker contains added calcium carbonate, which during cement hydration may form carbonated hydrated phases. There are indications in the literature that the $CaCO_3$ in these phases may be poorly crystallized or in a non crystalline phase [7,8]. Thus, this cement presents particular challenges to thorough characterization and is a good sample with which to determine the utility of various thermal analysis techniques to qualitatively and quantitatively determine the phase compositions during hydration. This cement system containing small amounts of additives and potentially some non crystalline components would present a particular challenge to characterization by X-ray powder diffraction, and we wish to demonstrate the additional information that is available by thermal analysis techniques.

2. Materials and methods

The cement used for the study will be referred to as MA cement and is produced in Brazil by Lafarge, code CP II F 32, and classified as blended Portland cement, type II [9]. Besides Portland clinker, it contains hydrated calcium sulfates and calcium carbonate [10], which are used to change the setting time of the cement [11].

The thermal analyses were performed from $28°C$ to $1000°C$, using 100 ml/min of air, as the purge gas, with a heating rate of $10°C$ min, in a simultaneous TG/DTA Seiko Instrument, model EXSTAR TG/DTA. The reference sample for the differential thermal analyses was alpha-alumina. DTG curves were obtained directly by the software of the equipment.

The analyses were done with MA cement and its pastes after 1, 4, 8, 14, 18, 24 h, 1 week and 4 weeks of hydration using a water/cement weight ratio of 0.5. The respective samples were named HYMA1H, HYMA4H, HYMA8H, HYMA14H, HYMA18H, HYMA24H, HYMA1W, HYMA4W. The pastes were prepared and kept in plastic bags which were sealed during storage for hydration.
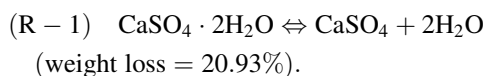
The dihydrated calcium sulfate (gypsum) in the cement plays an important role in the hydration process, forming in its initial stages hydrated calcium aluminate sulfate (ettringite) by reaction with the original calcium aluminate of the cement. The decrease of the content of gypsum, which can be measured from the areas of the respective DTG or DTA decomposition peaks, allows one to follow the progress of that reaction. The analysis after one hour of hydration was performed because the hemihydrated calcium sulfate present in the MA cement is totally converted to the dihydrated salt by that time [12,13], and the content of the dihydrate was considered as the initial reference value for a more correct analysis of its behavior during the cement hydration.

All the analyses were performed just after a drying step of the paste at $28°C$, in the equipment itself until constant weight conditions, using the purge gas as the drying agent. The preliminary drying step is necessary in order to avoid, in the thermal analysis curves, the overlapping effect of the step releasing free water with the dehydration step of the calcium silicate hydrate (tobermorite) [2]. The latter step begins at about $50°C$ under the operating conditions used. In the literature
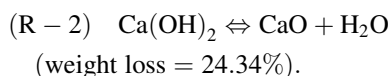
there are many methods of drying the paste before the analysis, such as the use of methyl alcohol or vacuum. The method applied here, which is actually an iso-thermal thermogravimetric procedure represents a simpler way to dry cement pastes than the existing methods, and avoids changing of some of the characteristics of the samples, as well as multiple weighing steps.

The contents of gypsum, calcium hydroxide and calcium carbonate were estimated from the weight losses measured from the TG curves between the initial and final temperatures of the corresponding DTG peaks, considering the following dehydration and decomposition reactions and theoretical weight losses:
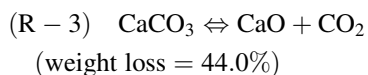
1. Dihydrated calcium sulfate (gypsum) dehydration [14]:

$$(R-1) \quad CaSO_4 \cdot 2H_2O \Leftrightarrow CaSO_4 + 2H_2O$$
(weight loss = 20.93%).

2. Calcium hydroxide decomposition [15]:

$$(R-2) \quad Ca(OH)_2 \Leftrightarrow CaO + H_2O$$
(weight loss = 24.34%).

3. Calcium carbonate decomposition [15]:

$$(R-3) \quad CaCO_3 \Leftrightarrow CaO + CO_2$$
(weight loss = 44.0%)

For the samples analyzed after 4 and 8 h of hydration, the gypsum content was estimated from the respective DTG peak area, which appeared clearly in the DTG curve, and not by the corresponding TG weight loss difference. In these cases, the difference, which represents the total area under the DTG curve, includes a significant weight loss due to the water released from the other hydrated components of the paste within the same temperature limits.

After short cure times, even drying the pastes prior to each analysis does not remove all interferences. There are still overlapping DTA or DTG peaks corresponding to the tobermorite gel ($3CaO \cdot 2SiO_2 \cdot xH_2O$) and ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) dehydrations, which occur, in this order, usually at the temperature range of 100–135°C. As will be shown, there are also dehydration reactions of other minor hydrated compounds, which result in continuously decreasing TG curves of the hydrated pastes, mainly up to 400–

450°C. Therefore, the total TG weight loss from ambient temperature to 400°C (subtracting, when appropriate, the water lost from the existing dihydrated calcium sulfate) and the subsequent calcium hydroxide decomposition weight loss (which ends by 500°C) were used to evaluate the degree of hydration of the paste.

As recommended by Taylor [16], for a better evaluation of the hydration process, all the estimated contents and the water released from other hydrates were calculated with reference to the final ignited mass of the pastes at 1000°C.

3. Results and discussion

Fig. 1 shows the TG, DTG and DTA curves of the MA cement and those of the paste after 1 h of cure (HYMA1H). It can be seen that the DTG curves present a much better base line than the DTA ones, and this was the case for all the samples. The identification of the main hydrated and carbonated phases can be made from their DTG dehydration or decomposition peaks. As shown in Fig. 1, the following were identified for the HYMA1H sample: a very small peak for CSH (tobermorite) dehydration between 40–60°C (showing that calcium silicate hydration has already begun at this stage); a significant peak at 110–145°C due to the regenerated dihydrated calcium sulfate (which was practically absent in the original MA cement, probably because it was decomposed during grinding in the mill [17], a small peak of calcium hydroxide decomposition occurring between 410°C and 460°C (due to a very small free lime content), and a significant peak at 520–730°C, due to the CO_2 released during calcium carbonate decomposition.

The respective weight losses can be obtained from the corresponding TG curves, which in turn allow the quantification of the respective phases. It is important to note that the high resolution of the thermal analysis experiment allows quantification of even very minor components. The latter are often not identifiable, and usually not quantifiable by X-ray diffraction experiments.

Taylor considers the process in terms of early, middle and late periods of hydration, with divisions at approximately 3 and 24 h after mixing [16]. Fig. 2 shows another typical hydration analysis which was
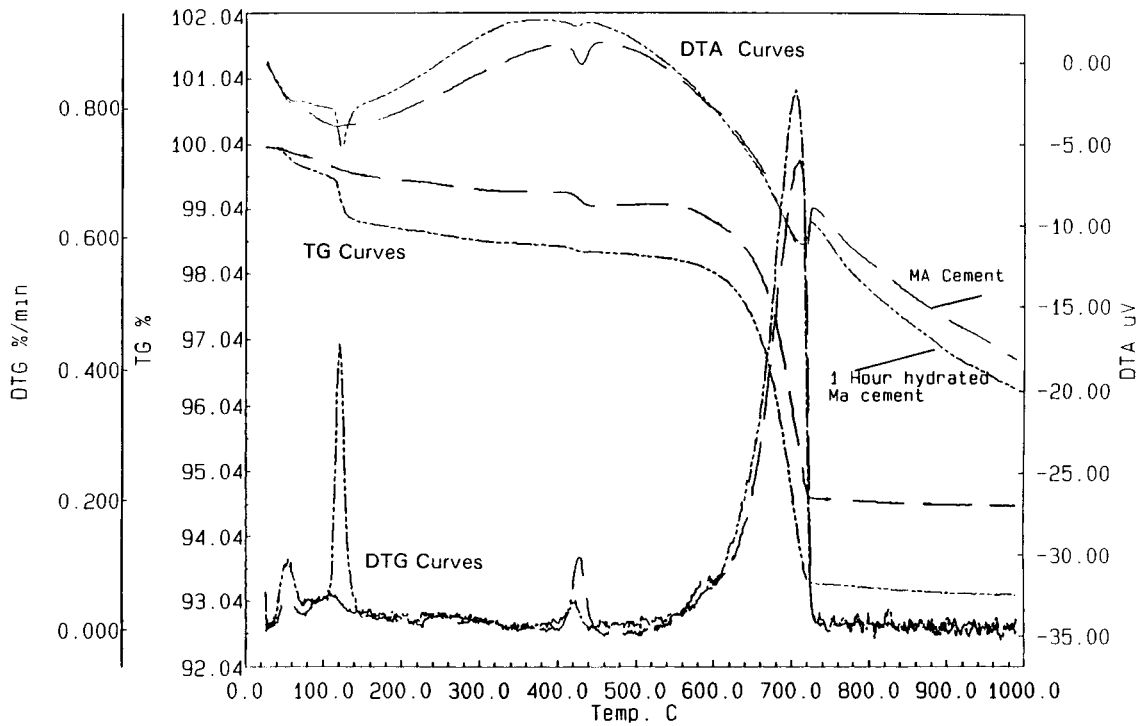
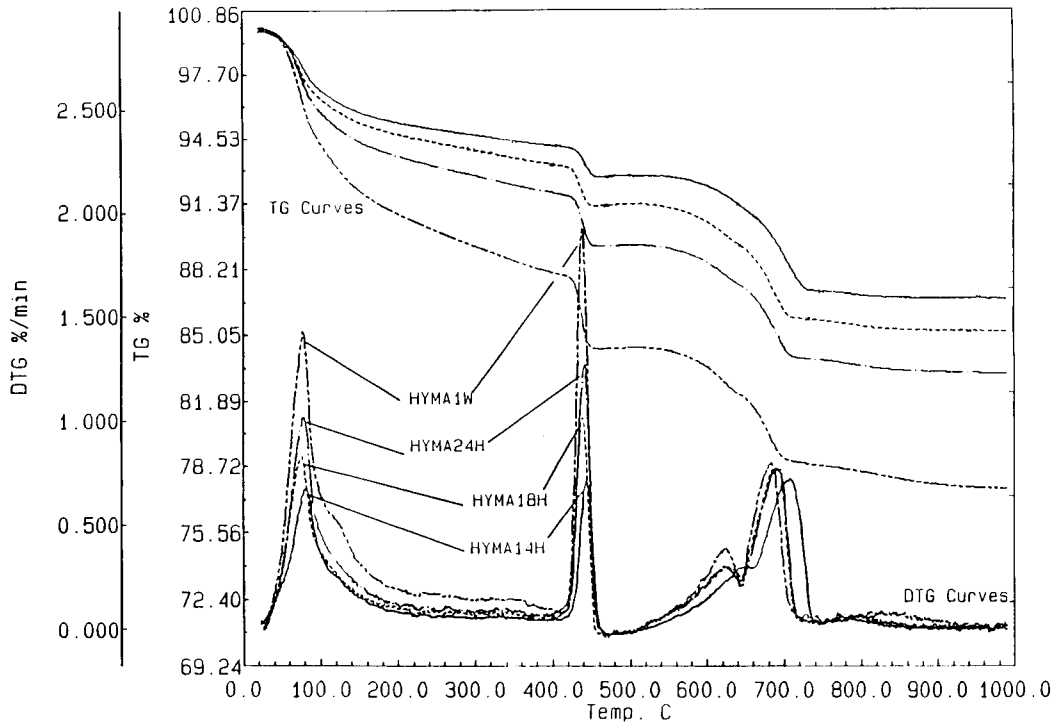Fig. 1. TG, DTG and DTA curves of the MA cement and of the paste after 1 h of cure.

Fig. 2. TG and DTG curves of pastes hydrated for 14, 18, 24 h and 1 week.

done by TG and DTG curves of cement MA pastes analyzed in the middle and at the beginning of the late period of hydration. It is interesting to note that the main hydration reaction of the cement, which is the calcium silicate hydration forming CSH gel (tobermorite) and calcium hydroxide, can be easily followed by the respective continuously growing DTG peaks, which show their maxima at about 95–450°C, respectively. Curves obtained at 4 and 8 h of hydration show clearly the DTG peak for the dehydration of the $CaSO_4 \cdot 2H_2O$ at 105°C. The DTG of the HYMA14H paste, when analyzed in a separate plot, shows a very small shoulder at this temperature indicating that some of the dihydrated calcium sulfate is still present. The same cannot be seen in the DTG curve of HYMA18H, apparently indicating that the dihydrated calcium sulfate was absent at this time of hydration. A pore solution analysis of a Portland cement paste, obtained with the same w/c ratio of 0.5, showed that sulfate ion concentration falls sharply at 12–16 h of hydration, and the solution thereafter is essentially one of alkali hydroxides [16]. It is important to note that the overlapping ettringite peak becomes more apparent at 135°C as a shoulder on the DTG curve, only after a week of hydration.

As shown in Fig. 2, as the hydration proceeds, the decomposition of the calcium carbonate maintains the same temperature range of occurrence as in the original cement and practically the same total peak area. However, it shows a continuous change in the DTG curve from a one-step to a two-step decomposition peak. For longer hydration times, mainly in the middle period of hydration, it can be seen that the peak which occurs at lower temperatures increases its area, probably due to the higher CO_2 mass evolved from carboaluminates formed during hydration, due to the significant calcium carbonate content in the original composition of the MA cement ([1], p. 160).

Fig. 3 shows the DTA curves corresponding to the TG and DTG curves in Fig. 2. As hydration proceeds, the two peaks of the $CaCO_3$ decomposition are not so well shown as in the DTG curves. The first peak shows a much smaller endothermic effect than the second one, and the ratio between their areas is much lower than the ratio between those of the corresponding DTG peaks.

The TG and DTG signs are direct and very fast measurements of the weight loss and its rate of occurrence during the analysis. They do not depend, as does the DTA sign, on the heat effect of the respective events, on the heat capacity of the residual products and on the permanent transient heat transfer state between sample and holder. From Figs. 1 and 3 it can be seen that the intrinsic properties of the products obtained during the thermal decomposition of the cement and pastes are also the cause of a non stable DTA base line, which makes the interpretation and quantification of the results more difficult. Thus, the calcium carbonate decomposition can be better evaluated by DTG than by DTA.
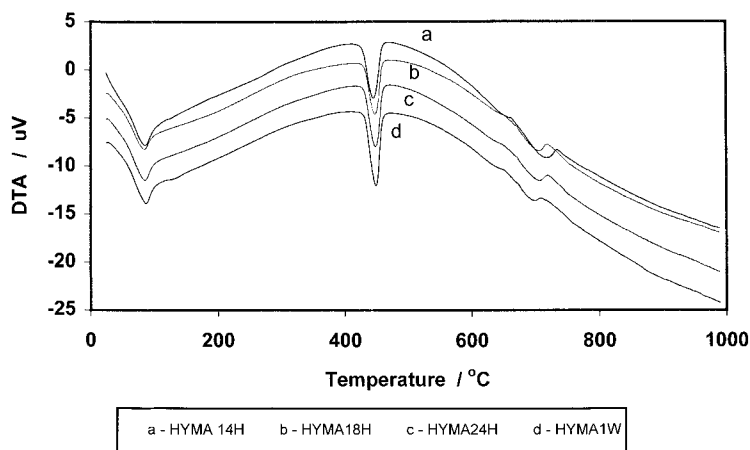

Fig. 3. DTA curves of pastes hydrated for 14, 18, 24 h and 1 week.

In the classic study of Greene [18], referred to by Ramachandran ([1] p. 94), after 7 days of hydration, the $CaCO_3$ decomposition peak is larger than it is after one day, because of the longer period of exposure to air. It is important to note that, although not shown by the author, in both cases the DTA curves actually show two consecutive overlapping peaks during that decomposition. When carboaluminates are formed in cement pastes [18,19], the corresponding DTA curves also show the same kind of peaks in the temperature range of $CaCO_3$ decomposition.

Cole and Kroone [7,8] have shown by X-ray diffraction, TG and DTA that in cement mortars cured in air, CO_2 is chemically bonded largely as poorly crystallized vaterite, aragonite and calcite, the decomposition of which would be represented by the smaller endothermic effect seen in carboaluminated pastes at 600–750°C. The peak with a more intense effect at 800°C, could be attributed to the decomposition of a well-crystallized calcite. The area of a DTA peak due to the combustion or thermal decomposition of a product is directly proportional to its mass and to the corresponding enthalpy change per unit mass (ΔH) of the transformation. This fact may be used to get the proportionality constant between total enthalpy change and DTA peak area for specific operating conditions of the DTA, using standard product(s) of known ΔH [20]. Thus, after this calibration procedure, the mass of a product in a sample may be estimated dividing the measured total enthalpy from a DTA peak area by the specific ΔH of the corresponding combustion or decomposition.

Chemical analysis of Portland cement mortars as well as of calcium silicate hydrates usually show higher total $CaCO_3$ contents than those estimated by the respective DTA analysis [7]. The ratio between the DTA peak area of the $CaCO_3$ phases is lower than the ratio of the corresponding DTG peak area, as can be observed comparing Figs. 2 and 3. The use of a lower area for the first DTA peak of the non crystalline $CaCO_3$ will result in lower estimated contents for it. Consequently the total content of calcium carbonate in the hydrated paste estimated by DTA will be lower than the actual one, as cited in the literature [7]. The CO_2 unaccounted for in the DTA would be that partly expelled at 600–750°C.

Thermogravimetry has an advantage since the mass of CO_2 released per unit mass of calcium carbonate does not depend on the various forms which can be present, but the ΔH of their decomposition probably do vary, and apparently, as seen in the results of this work, the poorly crystallized or non crystalline ones have lower ΔH than the well crystallized calcite.

El-Jazairi and Illston [3], using a semi-isothermal method of thermogravimetry and derivative thermogravimetry applied to high alumina pastes, also obtained DTG curves showing two overlapping peaks for the decarbonation step.

Bukowski and Berger [21], in a study on calcium silicate carbonation, also observed a small peak corresponding to poorly crystalline carbonate phase which decomposed at lower temperatures than the coarser and more stable $CaCO_3$. The latter is proposed to be formed by transformation and recrystallization of the former. In our case, well-crystallized calcite is present from the beginning in the blended cement clinker we are using.

These previous investigations provide an explanation for the two peaks observed in the decomposition of the present pastes and explain why no other carbonated crystalline substances were identified by X-ray diffraction in the hydrated pastes. Fig. 4 shows the X-ray diffraction patterns for 9 week hydrated MA cement pastes analyzed as formed and after heated isothermally at 200°C and 500°C, (samples HYMA9W, HYMA9W-2 and HYMA9W-5, respectively). These samples simulate three different conditions which occur during the thermal analyses. We sought to determine whether any other crystalline carbonate phases were formed during hydration and/or during the heating of the samples.

As can be seen, the main phases are portlandite ($Ca(OH)_2$) and calcite ($CaCO_3$). The former is practically absent in HYMA9W-5, and the latter was the only identified crystalline carbonate phase in all the samples. This indicates that the first of the $CaCO_3$ DTG peaks are probably due to the formation of a non crystalline calcium carbonate phase during the hydration process, as referred to in the literature studies cited above. The non crystalline $CaCO_3$ decomposes at lower temperatures causing the appearance of the two observed peaks in our DTG and DTA curves. Since it is non crystalline, it does not appear in the diffractograms, which show calcite as the only carbonated substance present.
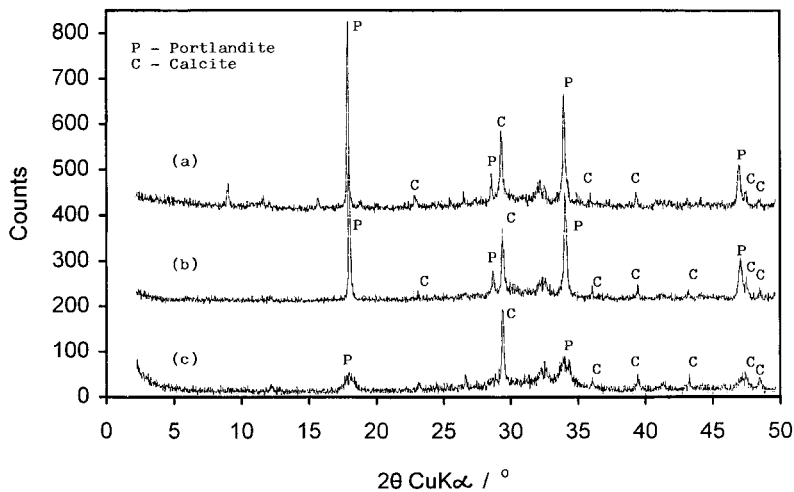
Fig. 4. XRD patterns of a 9 week hydrated paste as it is (a) and after heated isothermally at 200°C (b) and at 500°C (c).

Table 1 shows the weight losses due to the different dehydration and decomposition reactions occurring during the analyses, based on the dried weight of each sample. For the MA cement, which was not dried, the 0.79% of water lost from other hydrates includes 0.29% due to the water lost from the hemi-hydrated calcium sulfate present, formed during milling as discussed previously. For the hydrated pastes this loss from other hydrates includes the water released from CSH gel (tobermorite) and ettringite dehydration. The total TG weight loss at 1000°C, which was used to calculate ignited mass, represents the loss on ignition usually obtained by conventional procedures.

Fig. 5 shows the evolution of the contents, on ignited mass basis, of the main compounds that can be identified by thermogravimetry, which are present in the early and middle stage of hydration. The dihydrate of calcium sulfate, which is regenerated in the first hour, apparently is continuously consumed to form the ettringite in about 16 h. The total calcium carbonate content shows a small increase apparently due to some carbonation during processing. As shown in Table 1, the total CO_2 weight losses reach an approximately constant value after 8 h of hydration.

The calcium hydroxide content and the content of water released from other hydrates, including that from the CSH and ettringite, show a continuous

Table 1
Weight losses measured by TG and DTG based on dried samples

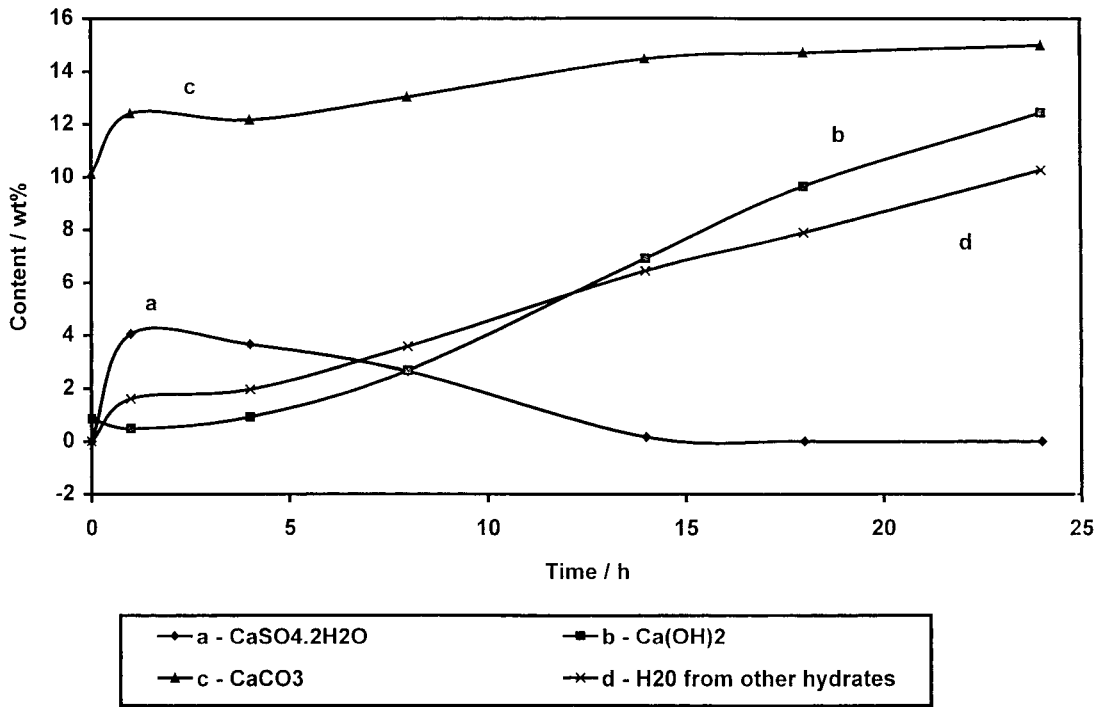| SAMPLE	Time of hydration	H_2O from $CaSO_4 \cdot 2H_2O$ (wt.%)	H_2O from $Ca(OH)_2$ (wt.%)	$CO2$ from $CaCO_3$ (wt.%)	H_2O lost from other hydrates (wt.%)	Total TG weight loss at 1000°C (wt.%)
MA Cement	–	–	0.21	4.45	0.79	5.45
HYMA1H	1 h	0.79	0.11	5.09	1.50	6.70
HYMA4H	4 h	0.71	0.21	4.97	1.82	7.09
HYMA8H	8 h	0.50	0.59	5.19	3.24	9.41
HYMA14H	14 h	0.03[a]	1.47	5.56	5.63	12.70
HYMA18H	18 h	–	2.00	5.52	6.73	14.81
HYMA24H	24 h	–	2.51	5.47	8.51	17.19
HYMA1W	1 week	–	3.60	5.62	11.92	22.36
HYMA4W	4 week	–	4.02	5.21	13.18	23.69

[a] Estimated.

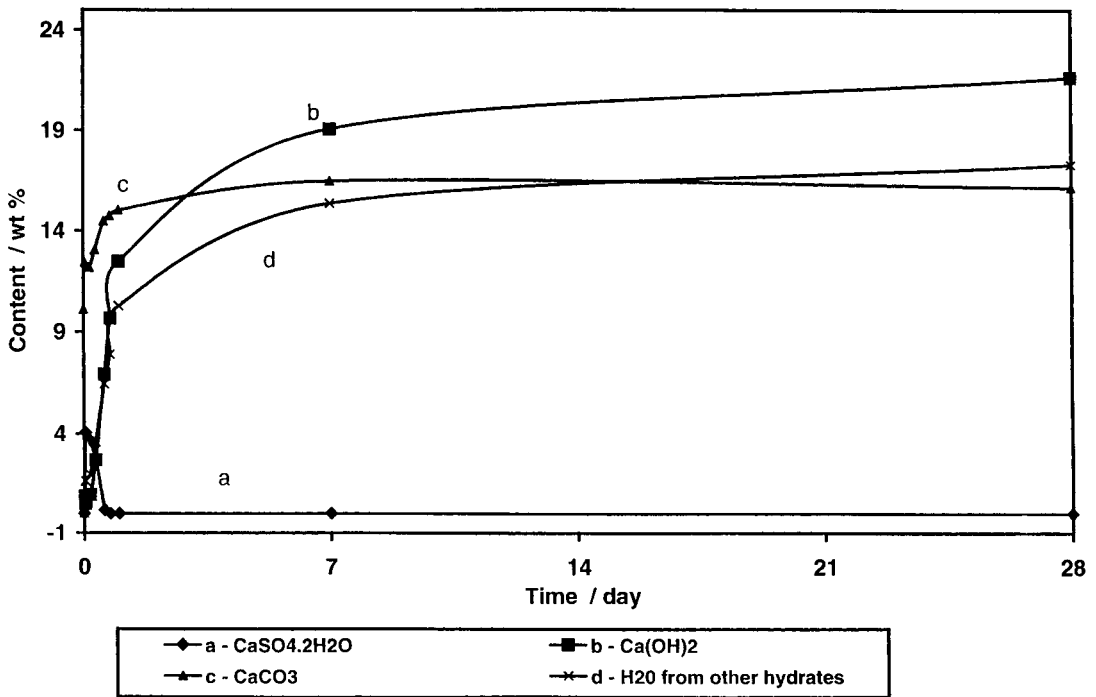Fig. 5. Composition data for MA cement pastes as a function of hydration time over 24 h.

Fig. 6. Composition data for MA cement pastes as a function of hydration time over 28 days.

increase in the middle period of hydration, and this increase is occurring at a much faster rate in the middle period than in the late period, as shown in Fig. 6. During the last three weeks, those contents increase in a similar way, indicating that the hydration seems to be mainly due to that of the tricalcium silicate, which forms calcium hydroxide and CSH. In this late period the total calcium carbonate content does not change significantly.

4. Conclusions

In order to dry samples to constant weight prior to thermal analysis, it is convenient and effective to use the purge gas at $28°C$. The sample can thus be dried within the thermal analysis equipment, avoiding external drying and weighing steps. The present work shows that such drying is very effective for cement pastes.

Thermogravimetry and derivative thermogravimetry are faster and more accurate methods than differential thermal analysis for a complete characterization of the hydrated pastes of Portland cement. The cement used in the present study, a blended cement containing calcium carbonate, presented more challenges to thermal analysis than the average cement. In addition to calcium carbonate, the original cement contained calcium disulfate in both hemihydrated and dehydrated forms, the former presumably formed during milling of the clinker. During hydration the dihydrated form was regenerated within 1 h, then subsequently consumed in the formation of other sulfate-containing phases in about 16 h.

During hydration the total equivalent calcium carbonate content is practically constant, but part of it becomes poorly crystallized, mainly during the middle period of hydration. This change is obvious in the TG and DTG curves, but is not apparent from X-ray diffraction.

This work has met the objective of providing, by thermal analysis characterization, a reference database of the hydration of the Portland cement blended with calcium carbonate, which is being used to solidify tanning wastes.

References

[1] V.S. Ramachandran, Applications of Differential Analysis in Cement Chemistry, Chemical Publishing Co., New York, 1969, pp. 92, 94, 160.
[2] W.J. Smothers, Y. Chiang, Handbook of DTA, Chemical Publishing Co., New York, 1966, p. 187.
[3] B. El-Jazairi, J.M. Illston, Cem. Concr. Res. 7 (1977) 247.
[4] B. El-Jazairi, J.M. Illston, Cem. Concr. Res. 10 (1980) 361.
[5] G. Kakali, S. Tsivilis, A. Tsialtas, Cem. Concr. Res. 28 (1998) 335.
[6] M. Moukwa, S. Farrington, D. Youn, Thermochim. Acta 195(1) (1992) 231.
[7] W.F. Cole, B. Kroone, J. Am. Concr. Inst. 31 (1960) 1275.
[8] W.F. Cole, B. Kroone, J. Nature 184 (1959) 57.
[9] Comité Européen de Normalization (CEN), Ciments Bétons Platres Chaux 795 (1992) 118.
[10] Lafarge, Materials to Build the World, Lafarge Publication, Portuguese, Rio de Janeiro, 1998.
[11] R. Sersale, Aspects of the chemistry of additions, in: S.N. Ghosh (Ed.), Advances in Cement Technology, Pergamon Press, Oxford, 1983, p. 538.
[12] J. Dweck, Proc. 39th Brazilian Ceram. Congr. 2 (1995) 1052.
[13] J.H. Norton, Fine Ceramics, McGraw-Hill, New York, 1970, p. 111.
[14] J. Dweck, E.I.P. Lasota, Thermochim. Acta 318 (1998) 137.
[15] J. Dweck, P. Souza Santos, Cerâmica 37(250) (1991) 80.
[16] H.F.W. Taylor, Cement Chemistry, 2nd ed., Thomas Telford, 1997, p. 102.
[17] Lea's, Chemistry of Cement and Concrete, 4th ed., Arnold, London, 1998, p. 134.
[18] K.T. Greene, Proceedings of the fourth International Symposium on Chem. Cements, Washington, 1960, p. 359.
[19] E.T. Carlson, H.A. Berman, J. Res. Nat. Bur. Std. 64A (1960) 333.
[20] R.W. Soares, V.J. Menezes, M.V.A. Fonseca, J. Dweck, J. Thermal Anal. 49 (1997) 657.
[21] J.M. Bukowsky, R.L. Berger, Cem. Concr. Res. 9 (1979) 57.