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THE EFFECT OF DIFFERENT BENTONITES ON CEMENT HYDRATION DURING SOLIDIFICATION/ STABILIZATION OF TANNERY WASTES

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Abstract

In the present work, a Portland cement blended with calcium carbonate is being used to study the solidification/stabilization (S/S) of a Brazilian tanning waste arising from leather production. Chromium is the element of greatest concern in this waste, but the waste also contains a residual organic material. Using thermogravimetry (TG) and derivative thermogravimetry (DTG) to identify and quantify the main hydrated phases present in the pastes, this paper presents a comparative study between the effects of Wyoming and Organophilic bentonites (*B* and *OB*) on cement hydration. Samples containing combinations of cement, *B, OB* and waste have been subjected to thermal analysis after different setting times during the first 28 days of the waste S/S process. Both bentonites affect the cement hydration, with no significant differences in hydration degree after 1 week. This work shows further examples of the great utility of thermal analysis techniques in the study of very complex systems containing both crystalline and amorphous mineral materials as well as organics.

Keywords: cement, DTG, hydration, solidification, stabilization, tannery waste, TG

Introduction

The solidification/stabilization (S/S) of hazardous wastes by cement-based binders is a technology that has been applied frequently to wastes containing heavy metals [1, 2]. When organics are present, organophilic clays are often suggested as solidification additives [3–5]. Thermal analysis characterization of cements and their hydration products has been done mainly by DTA [6], but increasingly over the last decades by conduction calorimetry, TG, DTG and DSC. The use of thermal analysis to study hydration of cements containing transition elements is more recent, and applications to stabilized/solidified waste systems have been relatively uncommon [7]. The hydration of the cement and of the cement pastes containing the waste and Wyo-

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ming bentonite were studied by TG, DTG and DTA in previous papers [8, 9]. This paper presents the study of the cement hydration during the first 28 days of the waste S/S process using organophilic bentonite (*OB*), and results are compared to those obtained in previous cases.

Experimental

A type II [10] Portland cement blended with calcium carbonate, produced in Brazil by Lafarge, code CP II F 32, referred to as MA cement, was used in this study. The waste is a residual mud produced in a tannery waste treatment station in Franca, SP, Brazil. The Wyoming bentonite (*B*) is from Sigma Chemical Corporation, St. Louis, USA, and the organophilic bentonite (*OB*) was prepared from *B* and tetramethylammonium chloride by a cationic exchange process detailed in literature [11].

After a previous drying step of the samples at 28°C, thermal analyses were performed up to 1000°C using 100 mL min^{-1} of air as the purge gas, with a heating rate of 10°C min^{-1}, in a simultaneous TG/DTA Seiko Instrument, model EXSTAR TG/DTA. Pastes composed of water (*W*), *MA* cement, *OB* and the tanning waste (*R*) were analyzed after 1, 4, 24 h, 1 and 4 weeks of setting. The water/cement ratio used to prepare the pastes was 0.5. The bentonite and waste contents in the pastes were 5 and 15% of the cement mass, respectively. As reference samples, pastes composed only of *W, MA* cement and *OB*, with the same relative amounts of *W, MA* and *OB* as those used in the solidified waste samples, were analyzed after the same times of setting. All the pastes were prepared and stored during hydration in sealed plastic bags. Results were compared with pastes obtained after the same processing time, in which *B* was used instead of *OB* and with pastes composed only of *MA* and *W*.

For each analysis, the dihydrated calcium sulfate, calcium hydroxide, calcium carbonate, tobermorite (calcium silicate hydrate gel) and ettringite (hydrated calcium aluminate sulfate), were identified from their dehydration or decomposition step DTG peaks during analysis.

Results and discussion

Figure 1 shows the TG, DTG and DTA curves of *B* and *OB* bentonite samples. Besides the different free water contents which are released up to 100°C, and dehydroxylation of the clays occuring after 500°C, the main difference between *B* and *OB* samples is the organic content burnout from *OB*, which occurs between 200 and 450°C and is characterized by the exothermal peak shown in the DTA curve. This is the same temperature range as the burnout of the organic content of the tanning waste [9].

Figure 2 shows TG, DTG and DTA curves of the pastes prepared with *MA* cement, *W*, and either *B* or *OB* after 24 h of setting (*MAB24H* and *MAOB24H*). As the pastes were previously dried, the mass losses up to 200°C, are due to the dehydration of the tobermorite gel and ettringite, which are two of the main hydrated phases [8] of the cement. During the solidification of the pastes, calcium hydroxide is also formed.

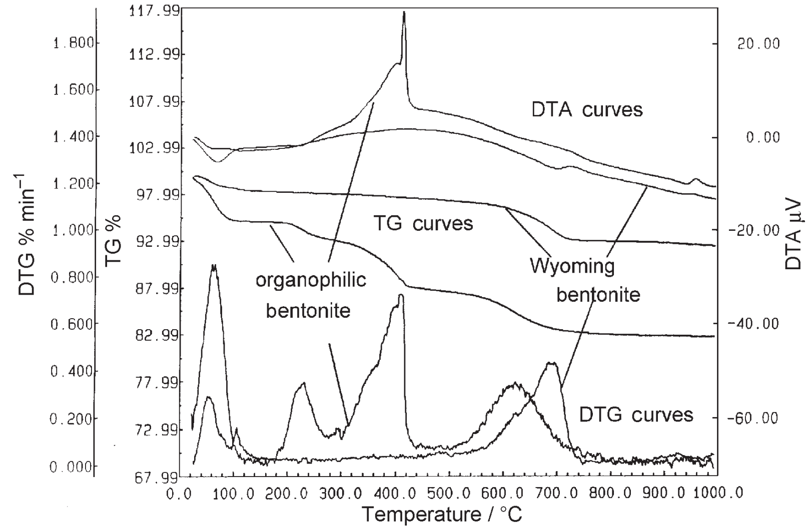

Fig. 1 TG, DTG and DTA curves of Wyoming and organophilic bentonites

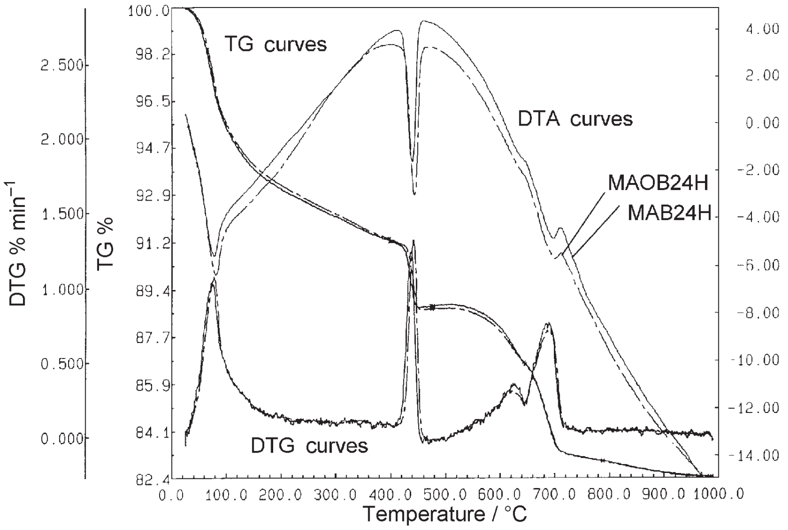

Fig. 2 TG, DTG and DTA curves of solidified pastes containing different bentonites after 24 h of solidification

The water lost from its dehydration, which occurs from 400 to 500°C during analysis, is slightly greater in the *OB* case, as shown from the corresponding DTG peaks. The two DTG peaks occurring after 500°C are due, respectively, to the non-well-crystallized and crystallized calcium carbonate phase decompositions [9], forming carbon dioxide in practically same contents in each case, as may be estimated from the mass percent loss obtained from the corresponding TG curves.

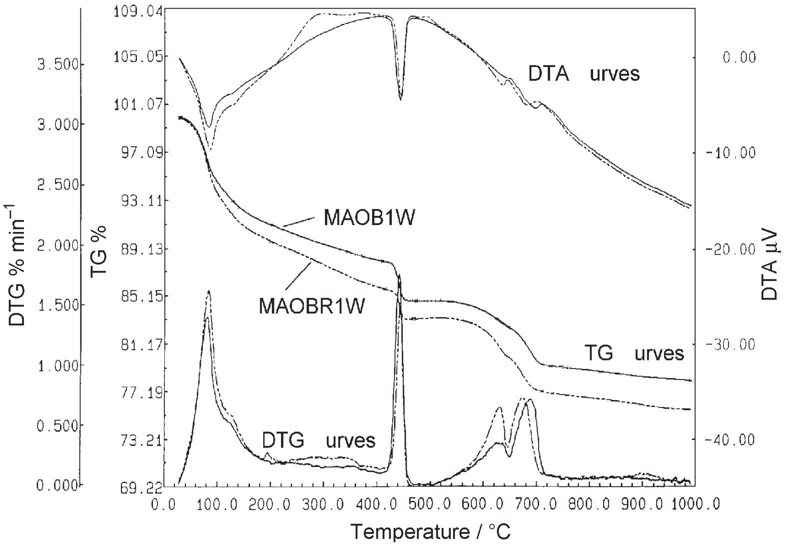

Fig. 3 TG, DTG and DTA curves of solidified pastes containing the waste and different bentonites after 1 week of solidification

Figure 3 shows a comparison between pastes solidified after one week, prepared with *OB* with and without *R* (*MAOB1W* and *MAOBR1W*). As the organic content in *R* is much higher than in *OB*, the *MAOBR1W* DTA curve shows clearly an exothermal peak due to its combustion, with a corresponding difference in the DTG curve behavior. The CO_2 from this combustion promotes a higher carbonation of the initial calcium hydroxide content of the paste during analysis. This results in a smaller DTG peak area for the hydroxide decomposition than in the *MAOB1W* case, and in a higher total CO_2 loss due mainly to non-well-crystallized calcium carbonate decomposition in the *MAOBR1W* case.

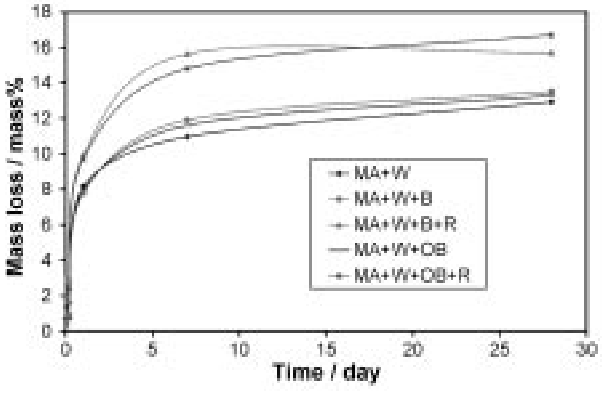

Fig. 4 Evaluation of the hydration degree as a function of solidification time, from the total mass loss due to tobermorite and ettringite dehydration

One measure of the degree of hydration of a cement paste is the amount of $Ca(OH)_2$ formed, and the latter can be determined from water loss from $Ca(OH)_2$ using TG. However, in the present case the $Ca(OH)_2$ is partially carbonated during analysis. Since the relative contents of the raw materials are different in the studied samples, to have a more reliable and common basis for comparison, the cement hydration degree was evaluated from the total water content lost from tobermorite and ettringite dehydration, which was estimated from the total TG mass loss up to 200°C, on an initial cement mass basis. Figure 4 shows the results, which indicate that the presence of the waste (*R*) enhances the hydration degree much more than either type of bentonite. The latter show similar effects on cement hydration.

Conclusions

Cement hydration during tanning waste solidification may be studied from TG and DTG curves, which allow the identification and quantification of the main existing phases after different setting times.

At 5% by mass with respect to the cement used, both *B* and *OB* have relatively little effect on the mineral composition of the setting Portland cement. However, 15% by mass of waste introduces a significant amount of organic and other material.

During analysis CO_2 is released from burnout of the organic content. The CO_2 reacts with $Ca(OH)_2$, reducing the amount of $Ca(OH)_2$ and increasing the amount of $CaCO_3$. In these cases the total water lost from dehydration of tobermorite and ettringite phases may be used to evaluate the cement hydration degree.

The presence of the waste significantly enhances the cement hydration from 24 h of cure up to 28 days.

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