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STUDY OF A BRAZILIAN SPENT CATALYST AS CEMENT AGGREGATE BY THERMAL AND MECHANICAL ANALYSIS

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Fluidized catalytic cracking units of refineries normally use zeolite catalysts to treat heavy oil fractions. This catalyst is regenerated continuously, but due to the reduction of its activity during the process, it is partially substituted by a new catalyst make-up. The spent residue has a high content of silicon and aluminum oxides and usually presents pozzolanic properties. This paper presents the study of a Brazilian spent catalyst, which is being tested as a pozzolanic aggregate in partial substitution to cement. Pastes were prepared with 15, 20 and 25% in substitution to cement mass and analyzed after 28 days of hydration.

Hydrated paste samples were analyzed by simultaneous thermogravimetry and differential thermal analysis, to quantify the calcium hydroxide consumption, as well as the content of other main hydrated cement phases. Compressive strength analysis was also performed after 28 days of hydration. Although, as spent catalyst content is increased, the pozzolanic activity is confirmed by the increase of calcium hydroxide consumption on cement mass basis, unlikely to other studied spent FCC catalysts, tested for the same purpose, the compressive strength of respective paste specimens decreases, due to the increase of other hydrated phases formation.

Keywords: *catalytic cracking, DTA, pozzolanic activity, residual catalyst, TG*

Introduction

Oil and natural gas supply 90% of total energy necessary to the planet and the tendency is their increase from 76 to 91 millions barrels per day in 2010 [1].

The feed of fluidized catalytic cracking units (FCC) at refineries consist of heavy residual products of petroleum distillation and are composed by several hydrocarbons and other impurities, including heavy metals [2–4].

The catalyst used in FCC units, after its regeneration process is returned to the reactor but it presents a permanent natural degradation due to coke obstruction of the pores of the zeolite structure, the main compound at the catalyst [5–7]. According to Dimon [8] the coke can be removed from the catalyst at 550°C, depending on the pore sizes. The spent catalyst is composed by metals, nitrogen, and sulfur and the initial raw material is considered mostly as zeolite, which presents high contents of aluminum and silicon oxides that may present pozzolanic activity and due to this property it can be used as partial cement substitute.

Canpolat [9] reported that natural zeolite and other pozzolanic materials contribute to the concrete strength, more than the cement strength only, providing physical and mechanical properties enhancing the cement characteristics. Silicon oxide present in zeolite reacts with calcium hydroxide, one of the cement products. This reaction may provide better properties to the solidified material.

This work presents the study of cement matrix behavior when spent catalyst is applied as a partial cement substitute. The matrix performance was evaluated by thermal and mechanical analysis with solidified samples after 28 days of hydration. These results complement the previous research of the authors [10], which showed that the spent catalyst presents pozzolanic activity in the early stages of cement hydration. This was also confirmed by the fact that after 24 h of reaction, the system cement+spent catalyst a decrease of calcium hydroxide content was determined quantitative and qualitatively by respective TG/DTG and DTA curves of the pastes.

Experimental

Materials and methods

The cement used was Portland cement type II blended with calcium carbonate, commercially known as CPII-E32 manufactured by Lafarge. The spent catalyst was provided by a Brazilian refinery, after its regeneration process in a fluidized catalytic cracking unit.

The paste compositions studied in this research were prepared with a water/solid material ratio of 0.5, with 15, 20 and 25% of cement substitution by spent catalyst, as shown in Table 1. These percentages were based on previous research results [10]. Two lots

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Table 1 Solid material compositions in pastes

Sample	Cement mass/%	Spent catalyst mass/%
P	100	–
P15X*	85	15
P20X	80	20
P25X	75	25

*X is related to the lot, 1 or 2

(1 and 2) of spent catalyst were used to compare results.

Spent catalyst chemical analysis was performed by X-ray fluorescence, in triplicate, in a Philips, PW 2400 equipment with Rh tube.

The solid raw materials were initially mixed and then manually was added the water, mixing until homogeneous pastes were achieved.

The solidified samples, original catalyst and spent catalyst as well, were analyzed by simultaneous thermogravimetric and differential thermal analysis (TG/DTA) performed from room temperature to 1000°C. 100 mL min^{-1} of nitrogen was used as the purge gas, with a heating rate of 10°C min^{-1}, in a simultaneous TG/DTA/DSC, TA Instruments equipment, model SDTQ600. The samples were prepared in plastic bags, which were sealed for 28 days. After this period they were ground and milled with an agate mortar and pestle to a particle size passing through sieve #100. The sample mass used in each analysis was about 10 mg. The analysis was performed in 3 phases: initial heating until 35°C; isothermal step for 60 min and a dynamic heating step until 1000°C at a heating rate of 10°C min^{-1}.

Compressive strength analysis was also performed, according to Brazilian norm: ABNT 7215/96 – Portland cement – Compressive strength determination. The prepared pastes were kept in cylindrical molds with 10 cm height and 5 cm diameter for 24 h and then removed to a wet chamber at 25°C with 100% humidity for a total of 28 days. The measurement occurs by the rupture charge, obtaining the individual strength, from Eq. (1):

$$IR = \frac{P}{As} \tag{1}$$

where P – rupture charge (kgf), As – section area of the sample.

The compressive strength is then converted to MPa.

Results and discussion

The spent catalyst characterization results are shown and discussed in following items. The X-ray fluorescence results are in Figs 1, 2 and 3.

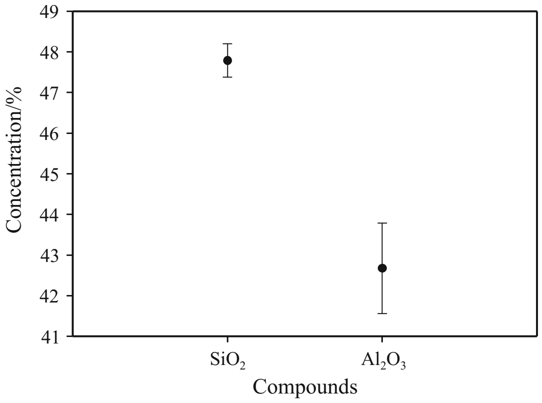

Fig. 1 X-ray fluorescence analysis results of the main oxides present in the spent catalyst

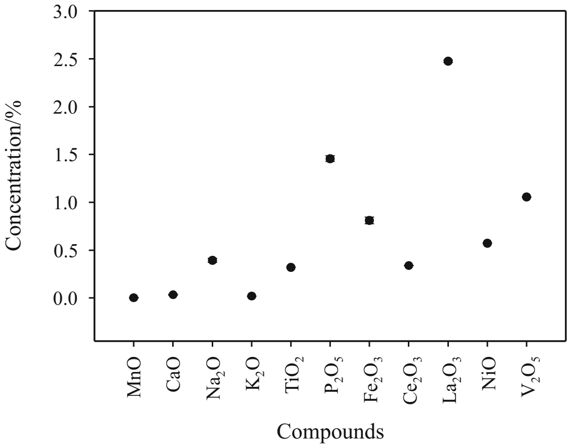

Fig. 2 X-ray fluorescence analysis results of other main oxides present in the spent catalyst

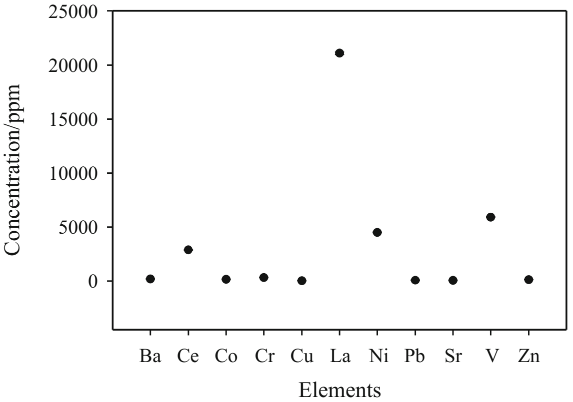

Fig. 3 X-ray fluorescence elementary analysis of the spent catalyst

Spent catalyst presents 47.5±0.41% of silicon oxide and 42.5±1.11% of aluminum oxide in its composition. These results show that this material has a high content of oxides, which may characterize pozzolanic material. This is due to the zeolite composition of the original catalyst.

Among the oxide analysis shown in Fig. 2, it can be observed that P_2O_5 and La_2O_3 present the higher concentrations. For NiO and V_2O_5, that could represent an environmental problem for this pozzolanic application, concentrations are 0.6 and 1.0%. Some other analyzed oxides were not listed, because they were under the detection limit of the equipment.

Silicon and aluminum elemental concentration results were not presented due to these elements content is above the detection limit of the equipment.

Original catalyst, spent catalyst and unhydrated Portland cement were analyzed by differential thermal analysis and thermogravimetry as received. Figures 4–6 show the TG, DTG and DTA curves of these analyses.

In Fig. 4 it can be observed that the original catalyst used in FCC units presents an initial mass loss until 200°C related to the environment exposition. This mass loss corresponds to 8.8% of the total mass, which according to Perraki [11] is due to the water released from the channel and cavities of the zeolite. Between 300 and 600°C the mass loss is due to the dehydroxylation of the mineral structure, which corresponds to the second endothermic peak, as shown by the DTA curve. The mass loss in this phase is 8.7%.

TG, DTG and DTA curves of the spent catalyst are shown in Fig. 5.

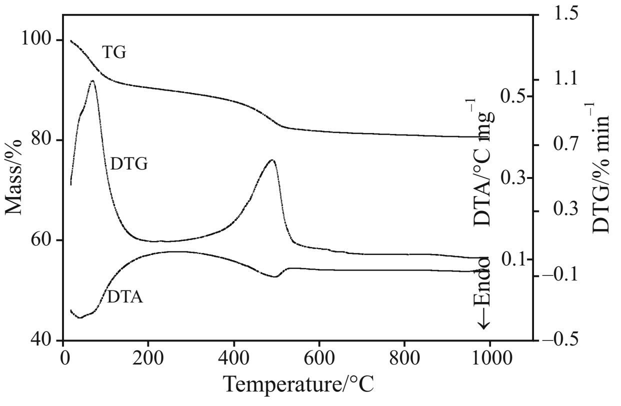

Fig. 4 TG/DTG/DTA curves of the original catalyst

The spent catalyst thermal analysis shows initially a mass loss of 3%, due to the water desorption from residual pores and channels, as observed from TG curve and the endothermic effect shown by the respective DTA peak until 200°C. After this temperature no significant mass loss is observed and the calcined residue present at 1000°C has 96.3% of the initial mass.

In the regeneration process at FCC unit, the temperature of regenerator attains 750°C, which enables practically the total coke removal in oxidant atmosphere [12, 13]. This explains the practical maintenance of the residual mass of TG curve after 200°C. When Figs 4 and 5 are compared, it can be noticed that the mass loss registered at the original catalyst TG curve, does not occur at spent catalyst TG curve for the higher temperature range, because dehydoxylation has already occurred at the regenerator processing temperatures.

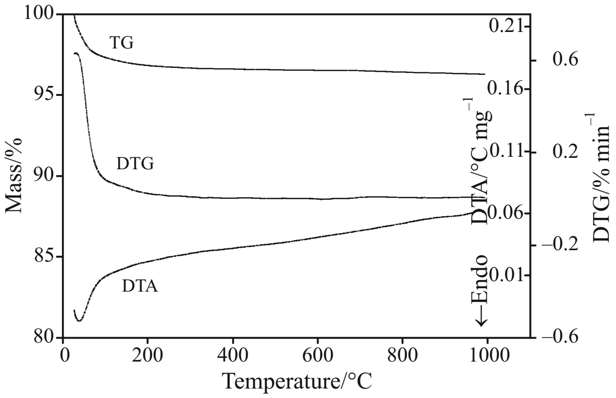

Fig. 5 TG/DTG/DTA curves of the spent catalyst

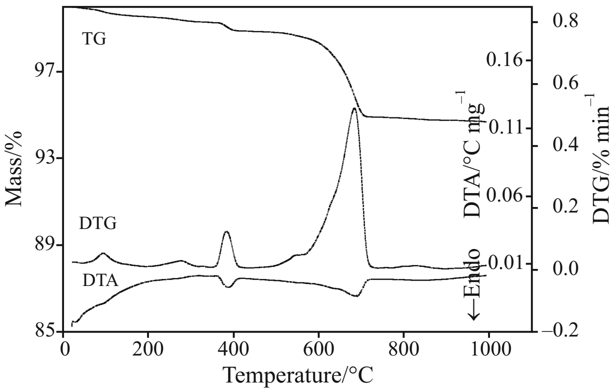

Fig. 6 TG/DTG/DTA curves of unhydrated Portland cement

As shown in Fig. 6, unhydrated Portland cement does not present a significant initial mass loss before 150°C. Between 350 and 500°C there is a dehydroxylation phase, corresponding to 0.5% of mass loss, due to the decomposition of a small calcium hydroxide ($Ca(OH)_2$) content in cement composition. The decarbonation of calcium carbonate, used as a blending aggregate in this cement, is also noticed by 4% of mass loss between 500 and 800°C.

Solidified samples were analyzed after 28 days of hydration. The respective TG, DTG and DTA curves and data presented in this work are shown on cement oxide calcined basis, as presented in the previous research [10], to have a same calculation basis to compare the differently composed pastes.

As shown in Fig. 7, Portland cement sample after 28 days of hydration presents an initial mass loss of 6.2%, which corresponds to free water lost during the isothermal step at 35°C for 1 h. During the following 10°C min^{-1} heating step, the first two overlapped main DTG peaks with endothermic effect until 200°C, correspond, respectively to the combined water released

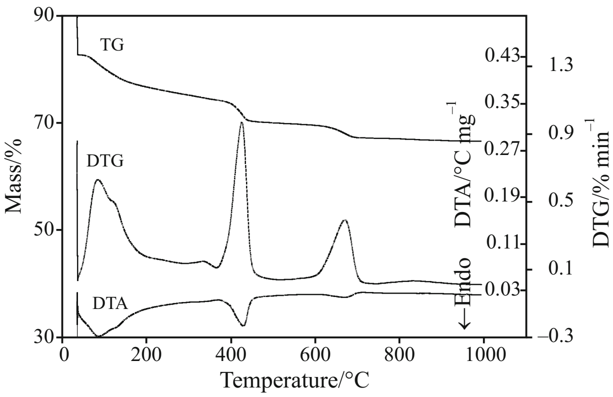

Fig. 7 TG/DTG/DTA curves of solidified Portland cement after 28 days of hydration

from tobermorite and ettringite phases dehydration, which were formed during cement hydration [14]. Respective percentage of mass loss is 5.8%.

Between 300 and 500°C it can be noticed the $Ca(OH)_2$ dehydroxylation phase [15, 16], which is also formed during the paste hydration process. The pozzolanic material activity is evaluated by the calcium hydroxide consumption [17]. In this study this decomposition step mass loss is important to compare (on calcined cement basis), the solidified samples containing spent catalyst and cement with the Portland cement hydrated sample paste. The decrease of this mass loss indicates calcium hydroxide consumption and the pozzolanic activity of the spent catalyst.

Calcium carbonate present in the sample is decomposed between 500 and 800°C.

Figures 8 and 9 present the thermogravimetric curves for solidified samples containing spent catalyst from different lots and the standard paste sample (P). Analyzing the samples containing 15, 20 and 25% of cement substitution by the spent catalyst, it can be observed a mass loss of free water at the isothermal step at 35°C followed by continuous mass loss steps, which present similar behavior for the two lots samples. Figure 10 presents the detail of DTG curves for lot 2 samples in the tobermorite and ettringite dehydration temperature range. Tobermorite DTG peaks show a higher production of this phase for 15% cement substitution. The ettringite DTG peak increases as cement substitution is increased, but DTG peaks for 20 and 25% cases are practically the same, indicating a practical limit for its formation. The increase of tobermorite and ettringite formation may be explained by pozzolanic reactions of the spent catalyst, due to respectively to its high contents of silica and aluminum oxides.

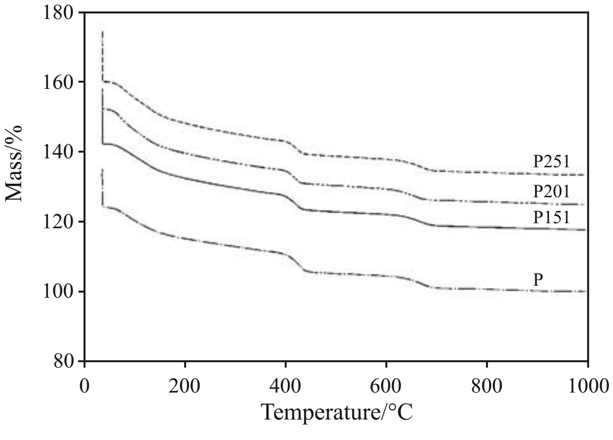

Fig. 8 TG curves of solidified samples with spent catalyst lot 1, after 28 days of hydration, on calcined basis

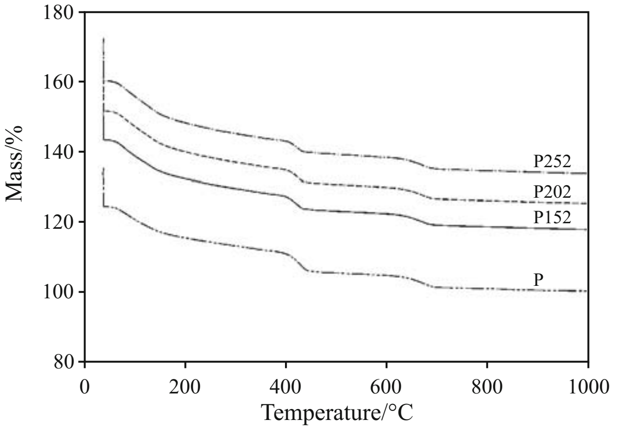

Fig. 9 TG curves of solidified samples with spent catalyst lot 2, after 28 days of hydration, on calcined basis

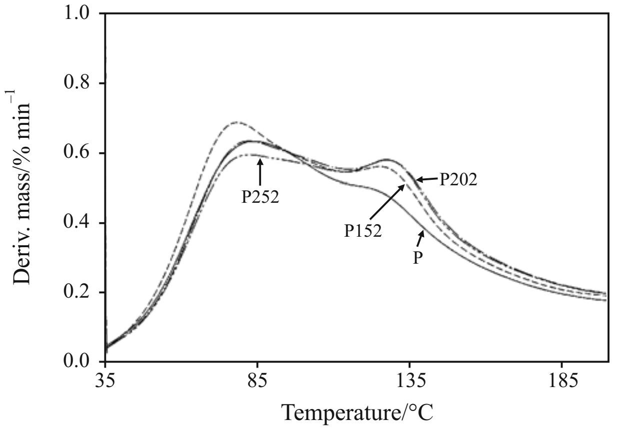

Fig. 10 DTG curves of solidified samples with spent catalyst lot 2, after 28 days of hydration, on calcined basis, at the temperature range of tobermorite and ettringite

From Figs 8 and 9 it can be noticed that the $Ca(OH)_2$ dehydroxylation occurs from 350 to 500°C. The higher is the spent catalyst content, the lower is the mass loss from this dehydroxylation step, which indicates lower calcium hydroxide content present in the paste. Between 600 and 750°C occurs the decarbonation of the $CaCO_3$ present in the pastes. Table 2 presents the mass loss data of the analyzed steps on calcined basis.

Table 2 Mass loss percentages during analyzed steps on calcined basis

Sample	Free water/%	Combined water from tobermorite ettringitede/%	Water from $Ca(OH)_2$/%	CO_2 from $CaCO_3$/%
P	9.3	9.0	6.4	3.8
P151	10.2	9.9	5.3	3.5
P201	4.8	12.7	4.6	3.5
P251	11.6	12.0	4.4	3.4
P152	7.3	11.2	4.8	3.6
P202	11.2	11.8	4.4	3.4
P252	9.8	12.2	4.0	3.5

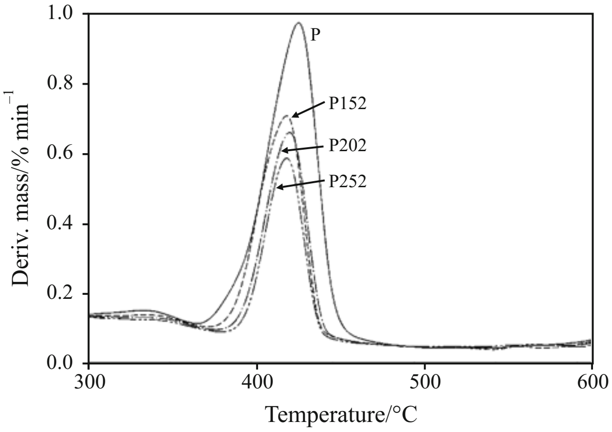

Fig. 11 DTG curves of solidified samples with spent catalyst lot 2, after 28 days of hydration, on calcined basis, at the calcium hydroxide decomposition temperature range

The reduction of calcium hydroxide (CH) as the spent catalyst content is increased in partial cement substitution, can be observed in Table 1 data, for both lot cases, from the decrease in the water lost in the CH dehydroxylation as substitution degree is increased. These results are due the pozzolanic activity of the spent catalyst, which reacts with the calcium hydroxide formed during cement hydration.

Calcium hydroxide consumption can be better seen from the DTG curves peaks shown in Fig. 11. The solid line, corresponding to the P sample, presents the highest peak and the increase of spent catalyst from 15 to 25%, decreases this peak gradually.

The pozzolanic activity of a material conventionally can be studied by the analysis of each additive to cement by the determination of lime consumed with different percentages of mineral added as function of time [18–20]. So the pozzolanic activity is evident by the fact that higher is the spent catalyst used to partially substitute cement, the higher is the calcium hydroxide consumption.

Usually thermal analysis curves are plotted by default on initial mass basis of the sample, as is the case of Figs 4 to 7, where TG curves express residual mass percentages on initial sample mass basis as a function of temperature. In the case where additives are used with cement, if initial mass basis curves are used to calculate mass losses, the higher is the amount of additive added, the higher can be the cement 'dilution' by the additive in the initial mass of the sample. In such cases, even if the additive has no pozzolanic properties, smaller mass losses due to CH dehydroxylation occur and smaller amounts of CH are calculated from the respective lower mass loss, due to the smaller content of cement in the initial mass composition.

It must be noted that to avoid this problem and to have a same mass basis of comparison, all the calculations of mass losses in the present paper were done on cement calcined basis, i.e. on the basis of the cement oxides mass present in the respective calcined samples at 1000°C, and non on the basis of the initial mass of each sample. Thus, all curves in Figs 8 to 11 were plotted on calcined basis by using calculation and plotting tools of the Universal Analysis software of the equipment, to have a same basis of comparison, to analyze those curves and to calculate data there from. Consequently, as indicated in Table 2, the smaller contents of CH (calculated on cement oxide calcined basis) for the samples in which the spent catalyst was added, when compared to the higher content of CH in the cement paste without spent catalyst (calculated on the same basis), do indicate that part of the CH was consumed by the pozzolanic activity of the spent catalyst.

Compressive strength analyses were performed after 28 days of hydration. Results are shown in Fig. 12.

From Fig. 12 it can be observed that there is a compressive strength reduction comparing the samples with spent catalyst data with the standard sample compressive strength. The reduction for samples P151 and P152 is above 30% compared to P sample. The samples prepared with the first lot of spent catalyst present a decreasing behavior on the compressive strength as the cement substitution degree increases. For lot 2, P202 sample presents a lower compressive strength than P152, but sample P252 presents almost the same value than P152.

The main difference noticed between the two lot sample characteristics was the difference between their particle size distributions, obtained by sieve

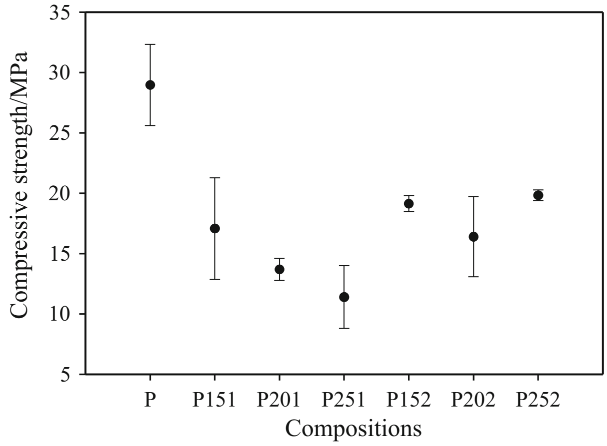

Fig. 12 Compressive strength of solidified pastes

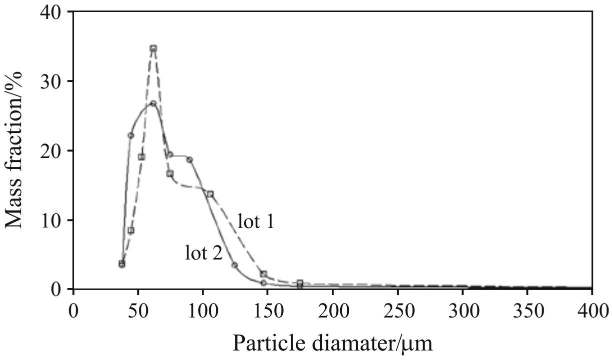

Fig. 13 Particle size distribution of the two lots

analysis. As shown in Fig. 13, lot 2 particles present a little better size distribution than lot 1 in the main 38 to 175 μ size range [21]. Besides this fact, lot 2 has 5.1 mass% of particles finer than 38 μ, whereas lot 1 has only 1.0 mass% in this range. A best particle size distribution and a higher content of finest particles, contributes to a better structure compaction of the solidified bodies. This may explain the difference in compressive strength results in each case.

The compressive strength reduction in both cases, when compared to the P case, may be due to the presence of compounds which came from the processed heavy oil fractions during the FCC process that contaminate the catalyst, such as Ni and V oxides. The presence of these oxides, as shown at Fig. 2 is low compared to SiO_2 and Al_2O_3 but it can interfere in the pozzolanic activity and compressive strength [22, 23].

Conclusions

Thermogravimetric analysis of hydrated pastes on calcined cement oxide basis allows a same basis of comparison to evaluate, after 28 days of hydration, the action of the spent catalyst in differently composed pastes.

The pozzolanic activity of the spent catalyst evaluated by thermal analysis was evidenced by the consumption of calcium hydroxide, formed during cement hydration.

The higher is the substitution of cement by the spent catalyst, the lower is the calcium hydroxide present at the different paste compositions after 28 days of hydration.

The reactivity of the spent catalyst with calcium hydroxide during cement hydration was also evidenced by a higher formation of tobermorite and ettringite phases than in the case of no cement substitution.

Although pozzolanic activity has occurred, the compressive strength of the pastes containing the spent catalyst was lower than the pastes formed with only cement and water. Some elements present in the spent catalyst composition like nickel and vanadium, may have limited the pozzolanic activity.

These facts indicate that when cement is partially substituted by spent FCC catalyst, the final mechanical property of the modified paste has to be determined for each case, because it may not necessarily be increased even when the spent catalyst presents pozzolanic activity.

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