POZZOLANIC PROPERTIES OF A RESIDUAL FCC CATALYST DURING THE EARLY STAGES OF CEMENT HYDRATION
Evaluation by thermal analysis

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The catalyst used in fluidized catalytic cracking (FCC) units of refineries after several recovery cycles in regeneration units, reduces its activity and it is partially substituted by new catalyst in the process. As it has a high silicon and aluminum oxides content, the pozzolanic properties of a Brazilian FCC spent residual catalyst, used in different substitution degrees to cement, were evaluated by three thermal analysis techniques during the early stages of hydration of a type II Portland cement. NCDTA curves show in real time that the residual catalyst, accelerates the stages of cement hydration. TG and DSC curves of respective pastes after 24 h of hydration evidence the pozzolanic activity of the waste, respectively, by the lower water mass loss during the dehydroxylation of the residual calcium hydroxide and by the lower dehydroxylation endothermal effect. Within the analyzed period, the higher is the cement substitution degree, the higher is the pozzolanic activity of the residual catalyst.
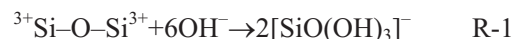
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Introduction

The original catalysts used in fluidized catalytic cracking units (FCC) at refineries consist basically of zeolite with other additives [1, 2]. After a thermal regeneration step to burn and eliminate the coke which is formed during the cracking process, a part of it, known as equilibrium catalyst, is taken out from the process as a catalyst waste because of the decrease of its activity. An equivalent amount of raw catalyst make up is done, to maintain the chemical activity of the catalyst which is recycled to the cracking step. The residual solid waste, which has a high content of silicon and aluminum oxides, may present pozzolanic characteristics and can be useful when applied in substitution to cement [3–6].

When zeolite is applied as a substitute to cement, the hydration process is more complex with change of conditions, kinetics and various reaction products are formed. These characteristics may affect the compositions and the properties of the hydrated cement [7]. The calcium hydroxide (CH), formed from the hydration of calcium silicates present in cement composition, reacts with pozzolanic materials, producing stable compounds like calcium silicate and aluminate hydrates with cementitious properties [8]. According to Perraki [9], in the basic media of cement hydration, the silicate or aluminosilicate structure present in pozzolanic materials is broken and depolymerized and may be dissolved by reactions R-1 and R-2. Thus,

Ca^{2+} ions react with the dissolved monosilicates and aluminate species forming calcium silicate and aluminate hydrates, in a similar way to cement component hydration products.

$$^{3+}Si–O–Si^{3+}+6OH^-\rightarrow 2[SiO(OH)_3]^- \qquad R\text{-}1$$

$$^{3+}Si–O–Al^{3+}+7OH^-\rightarrow [SiO(OH)_3]^-+[Al(OH)_4]^- \quad R\text{-}2$$

The pozzolanic activity of an aggregate in a cement/aggregate composition is characterized by the higher final mechanical resistance [10–12] due to the formation of the new hydrated phases, or from the lower CH content of the hydrated sample after pozzolanic action. In both cases, the results are compared to respective data of a cement hydrated sample without the aggregate after the same time of hydration. Due to the partial consumption of the CH formed during cement hydration by the pozzolanic aggregate, the CH content in the hydrated sample, can be directly determined from the respective TG curve on cement mass basis, at the end of a same hydration time, from the water lost during residual CH dehydroxylation during the analysis or from the lower endothermal effect of CH dehydroxylation during DTA analysis of the hydrated sample [13–15]. The pozzolanic action can also be measured from the Frattini test [16], by the calcium content of an aqueous solution where the cement/aggregate sample is maintained at least 8 days in contact with water at 40°C. In this case, the pozzolanic activity is evidenced, when the calcium

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content of the resulting solution is lower than the respective saturation calcium content curve, at the same hydroxide ion content of the solution.

The pozzolanic activity depends on type of zeolite used which may or not present cation exchange capacity of compounds with calcium present into cement [17]. When pozolans are applied with cement their behavior depends on cement and pozzolan composition and on the pozzolan/cement ratio. Their activity may not necessarily occur in the early stages of hydration, even when it occurs after some days of hydration [18]. This fact is important for civil engineering applications, because it is related with the changes in the setting process of the paste or mortar where the pozzolanic aggregate is used.

In this paper it was evaluated the pozzolanic activity of a spent catalyst of a FCC unit of a Brazilian refinery, during the early stages of cement hydration, considering that the original zeolite, which was deactivated during the refinery process, may also have reduced its pozzolanic activity during this period. By non-conventional differential thermal analysis (NCDTA) of the cement/spent catalyst compositions, the exothermal evolved heat was compared to that of the sample containing only cement and water. At the end of 24 h of hydration, the pozzolanic action was also analyzed by thermogravimetry (TG) and differential scanning calorimetry (DSC), from respective data of the residual CH dehydroxylation step. The effect on the setting time was analyzed as well, to know the influence on the structural mechanical properties during this period.

Experimental

Materials and methods

A commercial Portland cement type II, (named as P) blended with calcium carbonate [19–21] and a residual catalyst (CE) were used, this one supplied by a Brazilian refinery. The spent catalyst consists of a fine powder, which presents 65.7% of its particle sizes between 38 and 75 µm. Different pastes were prepared with a total water/dry material ratio of 0.5 and with 0, 5, 10, 15, 20 and 30% of cement substitution by the residual catalyst. They were named respectively as P, PCE5, PCE10, PCE15, PCE20 and PCE30. The total mass of solids was always 100 g.

The NCDTA system presents the same principle as DTA but with no external heating or cooling system. The temperature difference between the sample and a reference is measured in real time. Both samples and reference are kept in a closed polystyrene flask maintained in a styrene foam cup. The inert reference consists of a previously solidified cement paste with

more than 28 days of hydration. Respective thermocouples are inserted into the sample and reference inside the cup. The temperature data are collected through a Vernier Lab Pro interface, which sends them to a computer being registered as a function of time. More details of the measuring system can be found in a previous paper [22]. The total evolved heat on cement mass basis was estimated from the accumulated NCDTA peak area. The samples were prepared into the polystyrene cup, mixing the cement and residual catalyst and adding this mixture to water.

To evaluate the influence on setting behavior, Vicat needle test was performed according to the Brazilian Standard Method NBR 11581-MB 3434/91 [23]. Three different compositions were analyzed, containing 0, 15 and 20% of cement substitution by the spent catalyst.

Simultaneous thermogravimetric and differential scanning calorimetric (TG/DSC) analyses were also 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/DSC, TA Instruments equipment, model SDTQ600. The sample mass used in each analysis was about 15 mg taken from P, PCE5, PCE10, PCE15, PCE20 and PCE30 solidified samples, which were analyzed after 24 h of hydration.

Chemical analysis of the cement and spent catalyst was performed by X-ray fluorescence, in a Philips, PW:2400 equipment with Rh tube. The latter was also analyzed by X-ray diffraction using a Siemens/Brucker D5000 diffractometer. The radiation was K$_\alpha$ of copper of 1.542 Å, with steps of 0.050° (2θ) and time for steps of 1 s.

Results and discussion

Chemical compositions of the Portland cement [24] and of the spent catalyst as received are shown in Table 1. X-ray diffraction curve of spent catalyst is shown in Fig. 1. XRD curve shows the presence of faudjasite (F), silicium oxide (S) and aluminum silicate (Al) identified respectively, as the 38-0238, 45-0112 and 44-0003 products, according to International Centre for Diffraction Data. It can be seen that even after the catalyst is regenerated partially deactivated in the process, the faudjasite crystalline structure is still present, which may explain the pozzolanic properties during the early hydration stages as following discussed. A similar behavior was confirmed Grutzeck *et al*. [24] and by Martínez-Ramírez *et al*. [25]. According to Occelli *et al*. [26] during the FCC process, the zeolite modifies the caulim and aluminum structure, which promotes a catalytic activity reduction.

Table 1 Chemical composition of Portland cement (P) and spent catalyst (CE)

| Compounds	Spent catalyst (CE)	Blended cement (P)	Original cement without CaCO$_3$	Mineralogical composition of the original cement from BOGUE calculus	
				component	%
SiO$_2$/%	47.50	19.98	22.03		
Fe$_2$O$_3$/%	0.81	3.12	3.44	C$_4$AF	10.47
Al$_2$O$_3$/%	42.70	3.70	4.08		
CaO/%	0.03	62.80	63.01		
MgO/%	<0.01	3.10	3.42	C$_3$A	10.81
Na$_2$O/%	0.40	0.07	0.08		
K$_2$O/%	0.02	0.80	0.88		
TiO$_2$/%	0.32	nd	nd	C$_2$S	24.59
SO$_3$/%	0.005	1.78	1.96		
LOI	1.29	5.45	1.12	C$_3$S	51.13

nd – not determined
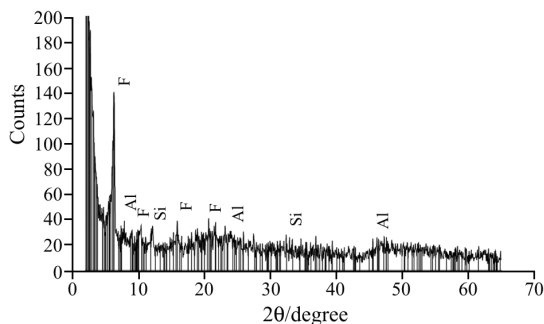
Fig. 1 X-ray diffraction curve of the spent catalyst, as received

Cement hydration reactions are exothermic and the highest peaks in NCDTA curves are due mainly to ettringite and tobermorite formation [27, 28], as shown in Fig. 2. It can be noticed that, the higher is the residual catalyst content, the higher is the first NCDTA peak, which occurs during the first hours of reaction, showing that residual catalyst components are reacting and contributing to the initial ettringite formation [27]. The composition containing 15% of CE (PCE15) presented a higher acceleration effect compared to 10 and 5% of CE samples (PCE10 and PCE5), obtaining a higher first peak 20 min before

PCE10 sample and one hour before sample PCE5. The same behavior was observed with the group of samples containing 20 and 30% of CE. Sample PCE30 presents the highest first peak. The second NCDTA peak is due to calcium silicates hydration, forming tobermorite [28]. All samples with partial cement substitution present a maximum of this peak occurring before the maximum of the same peak when only cement is hydrated (sample P), indicating that also an accelerating effect of this hydration stage occurs when the residual catalyst is present.

The total heat evolved up to 24 h of hydration of the samples P, PCE5, PCE10, PCE15, PCE20 and PCE30 was estimated by the respective accumulated NCDTA curve area on respective cement mass basis. The values were respectively, 77.0, 83.8, 90.7, 99.8 and 99.8 (in arbitrary units). The observed additional exothermal effects, with respect to the cement mass of each case, indicate that residual catalyst components effectively react in the solidifying media during the early cement hydration stages. PCE20 and PCE30 cases present at this time, the same total and highest evolved heat. As it can be seen in Fig. 2, during the second day, the hydration reactions occur in a much lower rate for all the samples.
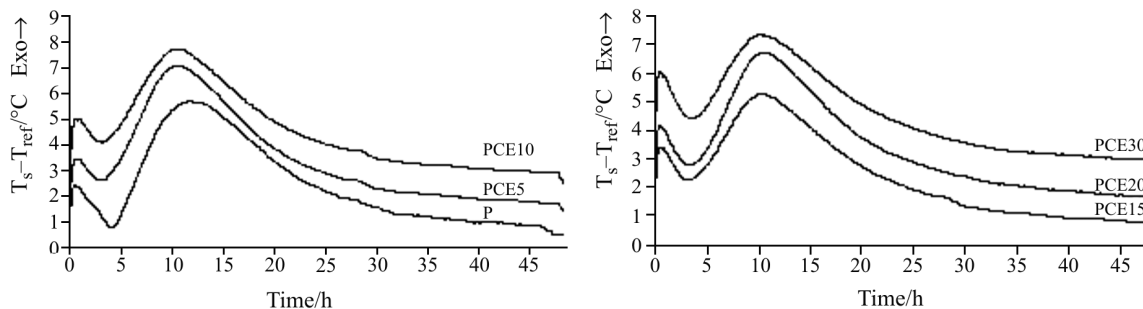
Fig. 2 NCDTA curves of the samples with 5, 10, 15, 20 and 30% of cement mass substitution by the residual catalyst

The effect of these reactions on setting was observed by Vicat Needle test [23]. As it is shown in Table 2, the higher the spent catalyst content, the earlier the setting begins to occur but the longer is the total setting time. This behavior shows that the pozzolanic properties of the spent catalyst accelerate the beginning of setting but, very probably, because of the minor metallic impurities, the final setting time is retarded [22].

Table 2 Setting time for P, PCE15 and PCE20 samples

Composition	Setting time (h:min)		
	initial	final	total
P	3:43	6:13	2:30
PCE15	3:28	6:38	3:10
PCE20	3:02	6:42	3:40

Figure 3 shows the TG curves of the residual catalyst and of the unhydrated type II Portland cement. After calcined at 1000°C, the residual oxides mass of each sample were, respectively, 94.69 and 95.75% of their initial mass. These values were used to calculate the several parameters on cement oxide calcined on the basis for the solidified paste samples after 24 h of hydration [29], by a procedure detailed in a previous paper [19].

The initial mass loss of the residual catalyst shown in Fig. 3 up to 300°C, corresponds to the free and adsorbed water loss. According to Perraki *et al.* [9] the mass loss is due to the hygroscopic water and the loss of the water residing in the channels and the cavities of the residual zeolite structure. Carbon and hydrogen contents of the residual catalyst, which were determined in a LECO CHN 1000 Analyzer, were, respectively 0.03 and 0.35 mass%. The nitrogen content also determined in the same equipment, was lesser than the smallest detectable content (0.17%). This indicates that: a) the hydrogen content is mainly due to the water content; b) in the catalyst regenerator of the FCC unit, the previous residual coke from the heavy oil fraction cracking process was practically all burned out; and c) the small mass loss after 300°C, may also be due to the volatilization or decomposition of other inorganic products. The type II unhydrated Portland cement presents 0.6% of mass loss up to 350°C due to the release of water from hydrated phases and a mass loss of 0.4% from 350 to 500°C due to the water released from the dehydroxylation of the CH originally present in the cement [27]. This cement also presents calcium carbonate [19], which was observed by the 4.3% of mass loss between 500 and 800°C, when the carbon dioxide is released during its decomposition.
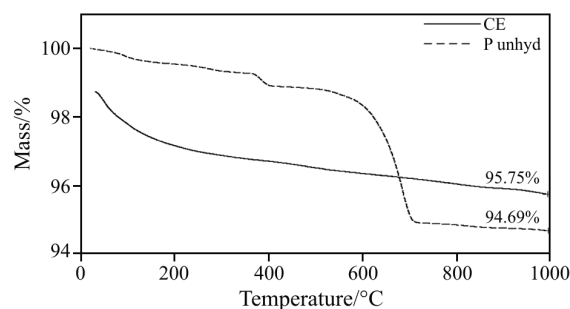

Fig. 3 TG curves of the residual catalyst (CE) and of the unhydrated cement in nitrogen atmosphere at a heating rate of 10°C min^{-1}

Figures 4 and 5 show, respectively, the TG and DTG curves of the hydrated cement (P) sample and of the samples prepared with different degrees of cement substitution, after 24 h of hydration, on respective cement oxide calcined mass basis. The TG curves of the hydrated samples initially present a mass loss of water from 35 and 200°C, due to the release of free water and to tobermorite and ettringite dehydration. Between 400 and 470°C, the dehydroxylation of calcium hydroxide occurs, which is one of the main products of cement hydration. The respective DTG peaks are shown in Fig. 4. The pozzolanic activity can be evaluated by the consumption of calcium hydroxide [13, 14]. The mass percent loss of the calcium hydroxide decomposition after 24 h of hydration in cement oxide calcined basis, calculated stoichiometrically from the water released during residual CH dehydroxylation [19], was 4.05, 4.06, 3.84, 3.73, 3.31 and 3.11%, respectively for P, PCE5, PCE10, PCE15, PCE20 and PCE30 samples. Thus, the pozzolanic activity of the residual catalyst during the early stages of cement hydration within the first 24 h is evidenced, by the fact that the higher is the cement substitution by the residual catalyst, the higher is the Ca(OH)$_2$ consumption.

Figure 6 presents the DSC endothermic peaks of the calcium hydroxide dehydroxylation step of the
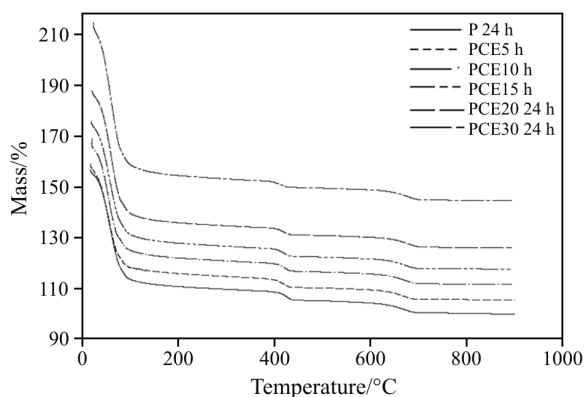

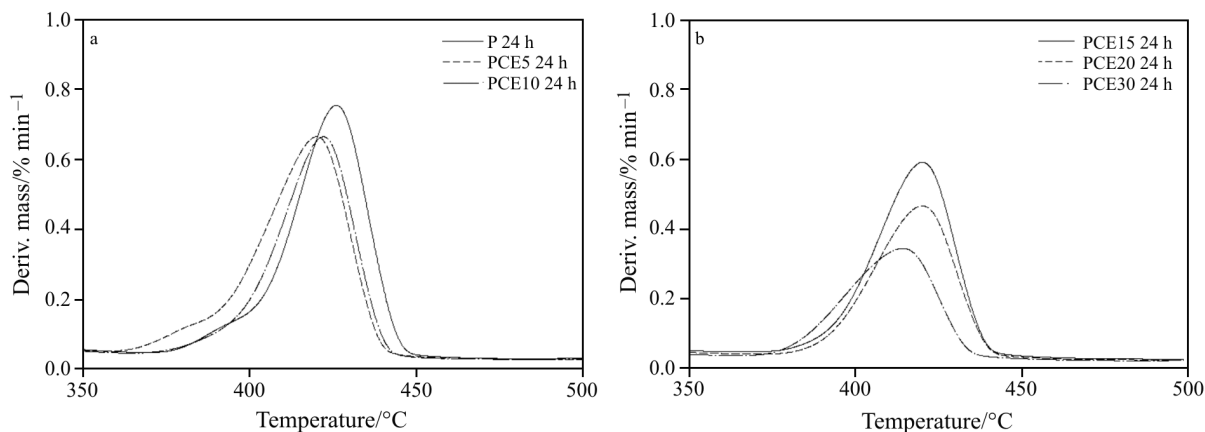**Fig. 4** TG curves of solidified samples after 24 h of hydration on cement oxide calcined basis

Fig. 5 DTG curves of solidified samples after 24 h of hydration on cement oxide calcined basis: a – samples P, PCE5 and PCE10; b – samples PCE15, PCE20 and PCE30
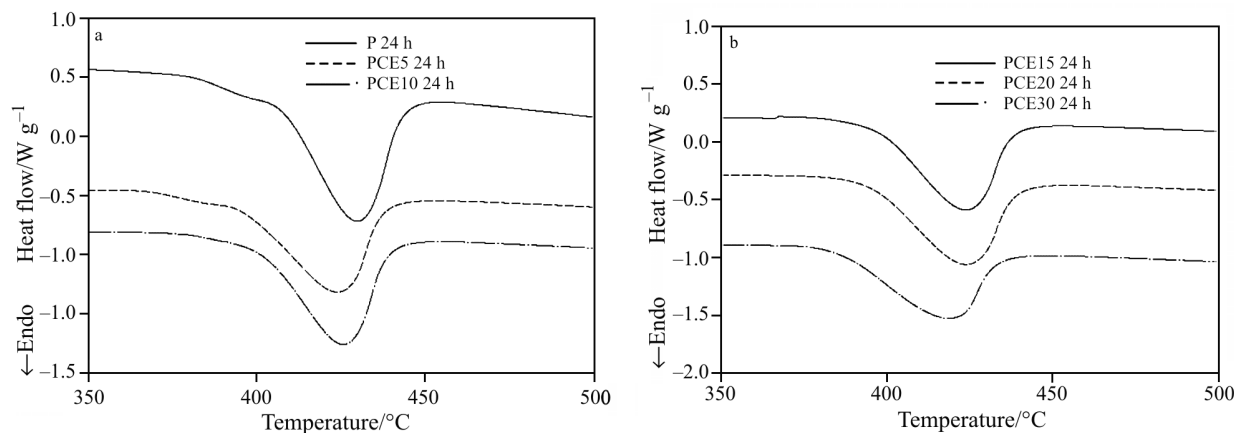

Fig. 6 DSC curves of the solidified samples after 24 h of hydration on cement oxide calcined basis: a – samples P, PCE5 and PCE10; b – samples PCE15, PCE20 and PCE30

samples hydrated for 24 h, on cement calcined oxide mass basis, which also confirm the pozzolanic activity of the residual catalyst in the pastes during the early stages of cement hydration. It can be observed that samples with 20 and 30% of substitution, present the lowest peak area, and consequently the lowest contents of the residual calcium hydroxide, indicating a consumption of the calcium hydroxide formed from cement hydration. The heat consumed for the residual CH dehydroxylation, per unit mass of cement oxides was 164.9, 138.7, 137.3, 121.5, 120.2 and 105.6 J g^{-1}, respecitvely for P, PCE5, PCE10, PCE15, PCE20 and PCE30 samples.

Conclusions

The spent catalyst presents pozzolanic activity during the early stages of the type II cement hydration, which also accelerates the beginning of setting.

By NCDTA it can be seen that the increase of cement substitution by the residual catalyst from 5 to 30% of the initial cement mass, increases the initial ettringite formation as well as accelerates the calcium silicate hydration during the early cement hydration stages.

TG analysis data of the pastes after 24 h of hydration, indicate that during this period, the higher is the cement substitution degree by the spent catalyst, the higher is the pozzolanic activity due to a higher consumption of calcium hydroxide.

DSC data also evidence the increasing pozzolanic action as the residual FCC catalyst content is increased, by the lesser heat consumed to decompose the residual calcium in the paste, after the same time of hydration than in the case with no cement substitution.

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