

A study of the particle size effect on the pozzolanic activity of an equilibrium catalyst

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A study by thermogravimetry was done to evaluate the influence of the particle size on the pozzolanic activity of a residual equilibrium catalyst from a fluid catalytic cracking unit of a Brazilian refinery. For this purpose, cement type II pastes with the same substitution degree containing coarse, medium, and fine fractions of the residual catalyzer were evaluated after 28 days of setting. Using thermogravimetric and derivative thermogravimetric analysis, the contents of total combined water and calcium hydroxide were determined. Comparing the results on initial cement mass basis of each sample with those of a control paste without any residual catalyst addition, it can be seen that the coarse and medium fractions present similar pozzolanic activity and the fine one presents a higher activity than the others due to its specific area and composition.

Keywords Equilibrium catalyst · Fluid catalytic cracking · Thermogravimetry · Pozzolanic activity

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Introduction

During fluid catalytic cracking (FCC) of oil heavy fractions, the catalyst not only suffers the reversible deactivation due to coke formation but also irreversible processes take place such as the sintering of the active component, collapse of the crystalline structure, and poisoning by deposition of metals oxide such as vanadium oxide. In order to keep the reaction performance the catalyst is replaced continuously little by little over time by new catalyst. The discarded catalyst receives the denomination “equilibrium catalyst” (ECAT). This exhausted material presents in its composition typically high concentrations of silica and alumina in such a way that it becomes with pozzolonic characteristics. However, the compositions and characteristics of this kind of material vary according to the refinery source and the type of processed catalyst.

Research focused in the use of ECAT as pozzolanic additive to cement has been done since the end of the 1990s. Chen et al. [1] have used ECAT in the form of fine collected by electrostatic precipitation. Su et al. [2, 3] analyzed its use in final cover cement. Antiohos et al. [4] proposed the use of ECAT as substitute of sand and also verified that the effect of the milling considerably improves the resistance of final product. Pundene et al. [5] verified that the addition of 5% of the used catalyst (ECAT) combined with additions of silica, and reactive alumina can also provide an increase in the resistance of the aluminous concrete. Pacewska et al. [6, 7] and Snellings et al. [8] have proven that through milling the pozzolanic activity increases due to the increase in the number of active sites capable of reacting with $\text{Ca}(\text{OH})_2$. Payá et al. [9, 10] have studied problems connected to the workability and pozzolanicity and have verified that the catalytic residue can present pozzolanic activity similar to metacaulinite's. The

effect of the ECAT thermal treatment in its pozzolanic activity was evaluated by Tseng et al. [11].

In a pioneering work in Brazil, we have evaluated in previous articles the possibility of use of ECAT originated from a Brazilian oil refinery as a pozzolanic material in partial substitution of the cement employed in construction concrete composites. Pinto et al. [12], Cherem da Cunha et al. [13], and Dweck et al. [14, 15] have evaluated the pozzolanic activity of the deactivated catalyst through thermal analysis techniques, having verified that an increase of ettringite formation and the acceleration of calcium silicate hydration take place, also showing that this technology can contribute for a decrease in the emissions of carbon dioxide in the atmosphere [16].

In this article, the influence of the particle size on the pozzolanic activity of an ECAT of another Brazilian refinery was studied by thermogravimetry (TG) and derivative thermogravimetry (DTG).

Materials and methods

Composites for the analysis were prepared using as basis 10 g of a mix with a proportion water/cement material equal to 0.5 that after addition of water was kept in air-tight closed plastic bags during 28 days. The standard control mix contained only cement and water. The mixes containing ECAT were prepared by replacing 24.53% of the original cement (in mass) by the ECAT having different particle sizes for each sample : between 74 and 90 μm (named coarse), between 44 and 74 μm (named medium), and smaller than 37 (named fine). This substitution degree of cement was used to be the same than that indicated to measure the index of pozzolanic activity of total ECAT sample by the Brazilian standard method NBR 5752, which determinates for this assay a 30% volume substitution of cement by the pozzolanic material. The corresponding cement mass substitution degree, which is 24.53 mass% in ECAT case, was maintained the same for all the pastes prepared with different particle size fractions to have the range of respective particle sizes as the only different parameter in this study.

All the hydrated samples were analyzed by thermogravimetry after drying at 35 $^{\circ}\text{C}$ for 1 h. The analyses were carried out using a TG/DTA instrument from TA Instruments, model 2960, heating at a rate of 10 $^{\circ}\text{C min}^{-1}$ from 35 to 1000 $^{\circ}\text{C}$ using 100 ml min^{-1} of nitrogen as a purge gas.

The determination of the total water was obtained by the loss of mass after the drying step (35 $^{\circ}\text{C}/1$ h) until the end of the decomposition of the calcium hydroxide. The water released in the decomposition of the calcium hydroxide is determined by the loss of mass that occurs between the

limits of temperature of corresponding peaks in the DTG diagram.

ECAT particle size fractions were obtained by conventional sieving. Surface areas of the different fractions were determined by a Nova 2200e Surface Area & Pore Size Analyzer from Quatachrome Instruments. Scanning Electron Microscope (SEM) images were obtained in a Field Emitting Scanning Electron Microscope (FESEM) (high resolution instrument) model JSM-7001F. Elemental analyses from the surface were made in the same SEM instrument using a Genesis EDAX equipped with a detector SDD (Silicon Drift Detector) with 10 mm window. The samples for the SEM and EDAX analysis were prepared by previous gold coating by sputtering (1 min).

Results and discussion

Figure 1 presents the particle size distribution of the ECAT particles for three samples. It can be observed that approximately 55% of the particles is in the range between 44 and 74 μm (medium fraction). This fraction, the one between 74 to 90 μm (coarse fraction) and the particles smaller than 37 μm (fine fraction) were used separately for the partial substitution of the cement in each composite to evaluate their effect on ECAT pozzolanic activity.

Figure 2 presents a typical result of curves TG and DTG of the cement composite with partial substitution using the ECAT fine fraction, using as basis the initial mass of the analyzed sample. The different losses of water mass are shown in the way that they were calculated for each analysis.

The initial mass loss in the curve TG occurs due to existent-free water in the composites. Between 35 and 200 $^{\circ}\text{C}$, the loss of mass in curve TG corresponds the water of tobermorite and ettringite decomposition, and between 370 and 470 $^{\circ}\text{C}$, in curve DTG it is possible to observe a

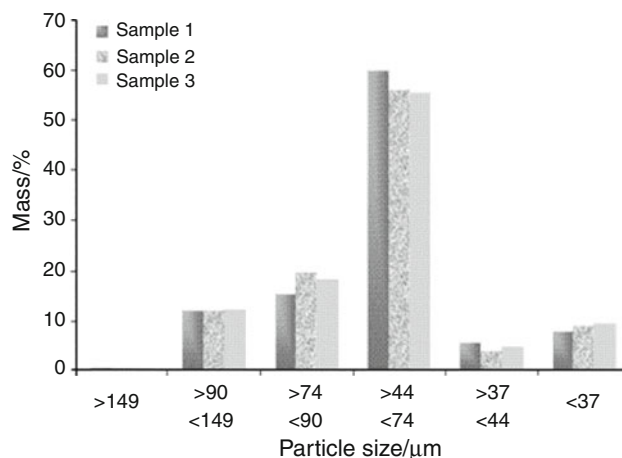


Fig. 1 Particle size distribution of the equilibrium catalyst

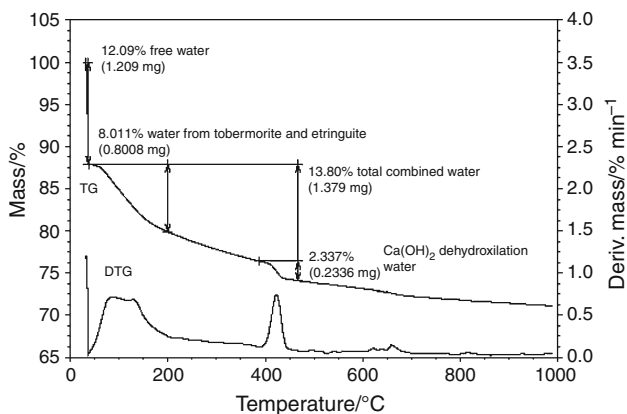


Fig. 2 TG and DTG typical curves of a cement paste containing fine fraction after 28 days of setting calculated on initial mass basis

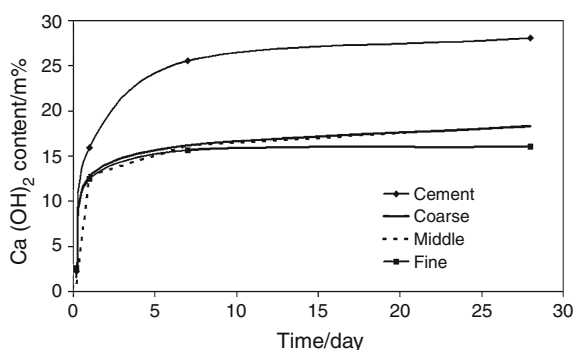


Fig. 3 Calcium hydroxide contents as a function of hydration time of cement control sample and composites containing cement and coarse, medium, and fine ECAT fractions as cement partial substitutes

corresponding peak belonging to the hydroxide calcium decomposition, with this data it is straightforward the determination in curve TG of the corresponding mass in this temperature range. Figure 2 TG and DTG typical curves of a cement paste containing fine fraction after 28 days of setting calculated on initial mass basis.

The process of calcium silicates hydration existent in the cement results in the formation of calcium hydroxide. The pozzolanic activity of the ECAT is quantified by the calcium hydroxide consumption during the pozzolanic reaction. Figure 3 shows the curves of percentages of calcium hydroxide present in each composite as a function of hydration time. The samples with ECAT fractions present a minor percentage of calcium hydroxide when compared to cement alone itself which gives evidence of the pozzolanicity of the same. The sample with the fine fraction still presents even a lesser percentage in comparison to the coarse and average fractions, showing its bigger pozzolanic activity.

The total water content in the samples is shown in Fig. 4. The samples with ECAT in their composition presented a greater percentage of hydrated products already after the first day of hydration which is evidence that

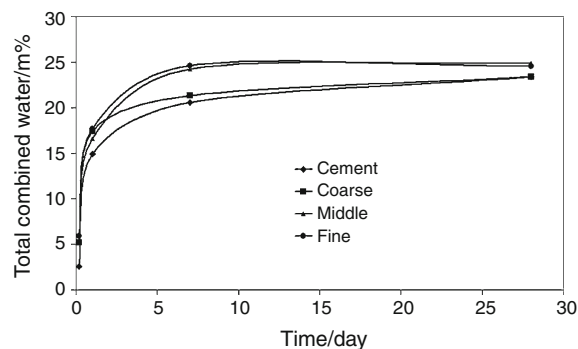


Fig. 4 Total combined water content during hydration of cement control standard and composites containing cement and coarse, medium, and fine ECAT fractions as cement partial substitutes

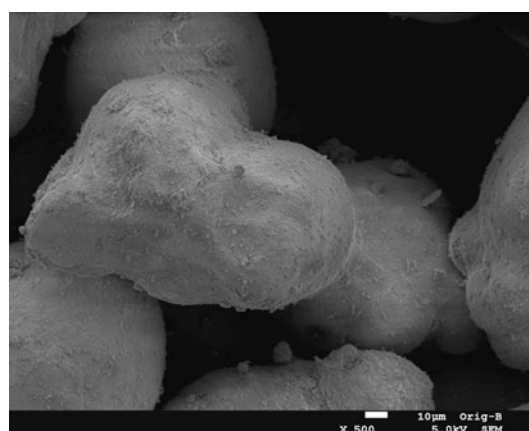


Fig. 5 Scanning Electronic Microscopy picture of the ECAT coarse fraction

there is more hydrated compounds formation resulting possibly in bigger mechanic resistance. The sample with the fine fraction of ECAT in partial substitution of the cement presents greater formation of hydrated products and a smaller amount of calcium hydroxide when compared with the samples containing average and coarse fractions of ECAT.

The SEM pictures shown in Figs. 5, 6, and 7 of the ECAT fractions demonstrate that the fine fraction presents more smaller particles and also more broken particles than the other fractions with bigger exposition of the more porous inside parts, which contributes for a bigger pozzolanic action of this fraction when compared with the samples from the average and coarse fractions.

Specific area of the coarse, medium, and fine particles by Multipoint BET analysis were, respectively, 156.02, 157.03, and 165.41 m² g⁻¹, which helps to explain the similar pozzolanic activity of the two former fractions and the higher pozzolanic activity of the last one.

Aluminum and silicium mass percent contents in the surface of the coarse, medium, and fine fractions, obtained

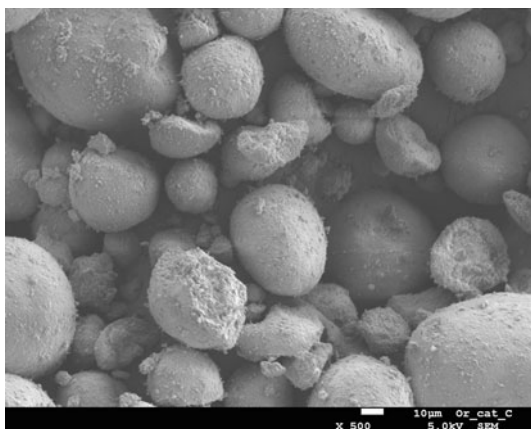


Fig. 6 Scanning Electronic Microscopy picture of the ECAT medium fraction

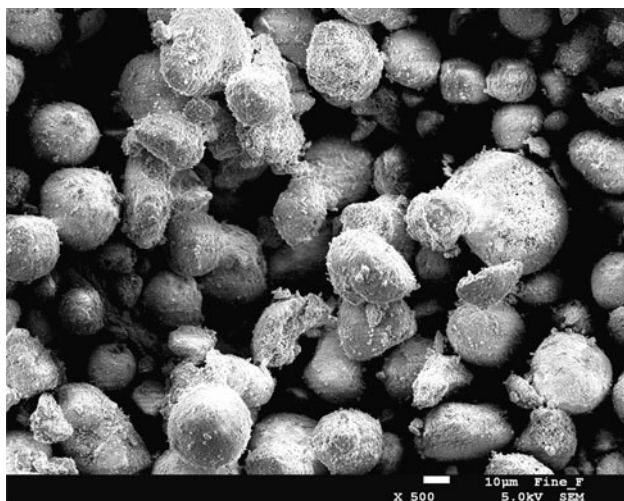


Fig. 7 Scanning Electronic Microscopy picture of the ECAT fine fraction

from EDAX, were respectively 25.53 and 29.38, 25.98 and 30.54, and 30.30 and 31.41%. This suggests that also the higher contents of aluminum and silicium and respective oxides can be another reason for the higher pozzolanic activity of ECAT fine fraction.

Conclusions

- The termogravimetric analysis based on cement in the initial mass of each composite makes possible the evaluation of the pozzolanic activity throughly the determination of the calcium hydroxide content in this calculation basis.
- Therefore, it can be observed that in the composites with partial cement substitution for residual catalyst there was a calcium hydroxide consumption when

compared with the standard control sample, which characterizes the pozzolanic activity of the catalyst, even when disactivated.

- While the fractions coarse and average of the residual catalyst had showed similar pozzolanic activity, the fine fraction presented greater activity after 1 and 4 weeks of the hydration.
- The biggest pozzolanic activity of the fine fraction of ECAT in relation to the other fractions is probably caused by its bigger superficial area and bigger surface contents of silicon and aluminum oxides.

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