

# EFFECTS OF RFCC SPENT CATALYST ON SOME PHYSICOMECHANICAL PROPERTIES OF PORTLAND CEMENT PASTE

ALI ALLAHVERDI, SHOKOUFEH VAKILINIA, POONEH GHARABEGLU\*

*Cement Research Center, School of Chemical Engineering,  
Iran University of Science and Technology, Narmak 16846-13114, Tehran, Iran*

*\*R&D Department, NIOEC Company,  
No. 263, Ostad Nejatollahi St., Tehran, Iran*

E-mail: ali.allahverdi@iust.ac.ir

Submitted December 13, 2010; accepted May 1, 2011

**Keywords:** Spent Catalyst, Portland Cement, Compressive Strength

*Spent catalyst from Residue Fluidized Catalytic Cracking (RFCC) unit of petroleum refining processes is an important waste material that should be treated in a suitable way. The main goal of this research is to evaluate the pozzolanic activity of RFCC spent catalyst and to investigate its effects on some physic-mechanical properties of Portland cement paste. Results show that workability and setting times of fresh pastes decrease by increasing the percentage of cement substitution. A substitution of cement by spent catalyst between 15% and 20% by weight could increase the 360-day compressive strength of the paste up to 108 MPa that shows 45% increase compared to the plain cement, i.e. 75 MPa. The interesting result is that it is possible to have high substitutions up to 40% without any reduction in 28-day compressive strength compared to plain cement. The RFCC spent catalyst is therefore a high quality supplementary cementing material.*

## INTRODUCTION

Disposal and possibly recycle or reuse of industrial by-products have become more important due to technological achievements and industrial growth. Spent catalyst from Residue Fluidized Catalytic Cracking (RFCC) unit of petroleum refining processes contaminated with some heavy metals such as vanadium and nickel, occurring on parts per million levels, should therefore be treated or disposed in a safe way. There are some practical ways for implementation of spent catalysts. Up to now, most of the waste catalysts are solidified and disposed as land-fills, however studies prove that this cannot be regarded as a safe disposal due to the presence of heavy metal contaminants. On the other hand, the chemical and mineralogical phase compositions of some spent catalysts are very similar to pozzolanic materials and therefore possible utilization of some spent catalysts as additives in Portland cement has been proposed [1-13]. Among industrial wastes, silica fume, fly ash, and blast furnace slag are the most successful examples. These materials have pozzolanic properties and react with calcium hydroxide produced in the hydration of the Portland cement phases to generate calcium silicate, calcium aluminate, and/or calcium aluminosilicate hydrates. These additional hydrates are the principal components responsible for the increase in the mechanical strength of the cement paste [2,5].

Recently, a number of papers have been published on the possible utilization of Fluidized Catalytic Cracking (FCC) spent catalyst as a pozzolanic material [1-13]. Pacewska et al [3] have studied the pozzolanic properties of this material using thermal and spectroscopic techniques and have concluded that its ability to react with calcium hydroxide is similar to microsilica. Paya et al [11] have also claimed a relatively high pozzolanic activity for ground FCC spent catalyst. Su et al [9,10] and Paya et al [7] carried out feasibility studies of reusing this spent catalyst as a supplementary cementing material. Their results indicate that replacements up to 20 % of cement or 10 % of fine aggregate are possible without sacrificing the quality of mortars.

If just considering chemical composition, RFCC catalyst seems very similar to that of FCC. However, it is notably different considering operating conditions. Since RFCC unit has been designed to crack heavier petroleum fractions at higher temperatures, the utilized catalyst must therefore be thermally more stable to resist higher temperatures up to 720°C [14]. RFCC catalyst is usually deactivated sooner than FCC not only due to higher process temperatures, but also due to higher concentrations of feed impurities including Vanadium. The Vanadium containing compounds of feed are decomposed and the Vanadium content is mostly converted to  $V_2O_5$ , which then reacts with water vapor to form  $H_3VO_4$ . This acid reacts with alkali-metals of

the catalyst and results in structural degradation and deactivation of the catalyst [15].

The purpose of this study is to evaluate the pozzolanic activity of RFCC spent catalyst. The effects of the spent catalyst on some basic physicochemical properties of Portland cement paste including workability, setting times, compressive strength, total 90-day shrinkage, water absorption, and total permeable pore volume are also studied. Laser particle size analyzer (Sympatec, GmbH, HDD), X-ray diffractometry (JEOL JDX-8030), FTIR (Shimadzu-8400S), Thermogravimetry (Netzsch model 429), and Scanning electron microscopy (Philips XL30) were the principal laboratory techniques used in this study.

## EXPERIMENTAL

### Materials

The materials used in this study include Type II Portland cement (in accordance with ASTM standard), and RFCC spent catalyst. Microsilica and metakaolin were also utilized as reference pozzolanic materials. The properties of the materials are presented in Table 1.

Knowing that particle size distribution of the spent catalyst could strongly affect both wet and dry properties of Portland cement, the spent catalyst was firstly ground in a laboratory ball mill for 100 minutes to obtain a relatively fine powder comparable to Portland cement. The particle size distribution of the catalyst powder was determined by a laser particle size analyzer (Sympatec, GmbH, HDD) and the values of specific surface area and bulk density of ground catalyst were measured in accordance with ASTM C204 and ASTM C188-95, respectively. Figure 1 shows the particle size distributions of spent catalyst before and after grinding respectively.

Before grinding, the particles of spent catalyst were bigger than those of cement and the dominating weight fraction was particles greater than 40  $\mu\text{m}$  with 82.5 % of the grains in the range 37.5-90  $\mu\text{m}$ . The spent catalyst is therefore better to be ground in order to increase its reactivity. After grinding, the weight fraction of particles less than 50  $\mu\text{m}$  has been increased. As seen, in the ground catalyst almost 95 % of the grains are in the range 5-90  $\mu\text{m}$  that is comparable to the particle size distribution of Portland cement.

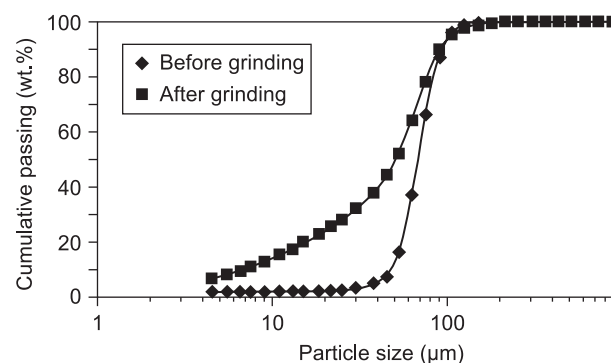


Figure 1. Particle size distribution of RFCC spent catalyst before and after grinding.

The spent catalyst was then characterized for its chemical composition. The results of chemical analysis determined according to ASTM standard C311 and the values of specific surface area and bulk density are shown in Table 1. The results of chemical analysis reveal that the catalyst is mainly made up of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . As seen, these two components account for over 95% of the total weight of the material. This catalyst is therefore relatively high siliceous and according to ASTM standard C618, it could chemically be considered as a relatively good artificial pozzolan.

Table 1. Properties of Portland cement, microsilica, and metakaolin.

Composition (wt%)	Cement	Microsilica	Metakaolin	Ground Spent Catalyst
$\text{SiO}_2$	20.26	96.12	65.81	58.43
$\text{Al}_2\text{O}_3$	5.43	0.82	27.42	37.32
$\text{Fe}_2\text{O}_3$	3.87	–	0.54	1.19
CaO	64.96	–	1.48	–
MgO	0.48	–	0.65	0.65
$\text{SO}_3$	2.09	–	–	0.20
$\text{Na}_2\text{O}$	0.27	–	0.32	0.82
$\text{K}_2\text{O}$	0.60	0.40	0.43	0.11
$\text{TiO}_2$	–	–	2.31	–
L.O.I	1.95	2.61	0.86	1.25
Free CaO	0.45	–	–	–
$\text{C}_3\text{S}$	54.54	–	–	–
$\text{C}_2\text{S}$	17.01	–	–	–
$\text{C}_3\text{A}$	7.84	–	–	–
$\text{C}_4\text{AF}$	11.78	–	–	–
Fineness ( $\text{m}^2/\text{kg}$ )	320 (Blaine)	18000 (BET)	11000 (BET)	315 (Blaine)
Density ( $\text{kg}/\text{m}^3$ )	3130	213	2880	2470

## Methods

The mineralogical phase composition of the catalyst was determined by the use of powder X-ray diffractometry. Pozzolanic activity of the spent catalyst was investigated based on thermogravimetric analysis of cured lime-catalyst paste. A thoroughly homogenized binary mixture of calcium hydroxide and spent catalyst at equal proportions was utilized for preparing a paste at a water-to-dry material ratio of 1. The paste was then stored at an ambient of  $N_2$  atmosphere at 60 °C for being cured. After given time periods, the paste was firstly dried with acetone and  $N_2$  gas and then utilized for measuring the amount of reacted calcium hydroxide by thermogravimetric analysis. FTIR studies were also carried out on the same paste sample after 7 and 28 days of curing in an atmosphere of more than 95% relative humidity at 25°C.

Binary cement mixes were designed and prepared with additions of 0 %, 5 %, 10 %, ... and 40 % (relative to the mass of dry binder) of ground spent catalyst used as a substitute for Portland cement. Water-to-cement ratio was taken constant at 0.40 for all the mixes to investigate the sole effects of the spent catalyst on wet and dry properties of the pastes. After preparing the pastes of different consistency, they were firstly characterized by determining their relative workability and initial and final setting times in accordance with ASTM C230 and ASTM C191 respectively. The pastes were then cast into specimens of  $2 \times 2 \times 2$  cm<sup>3</sup> in size. The molds were stored at an atmosphere of more than 95 % relative humidity at 25°C for the first 24 h and then the specimens were cured in water at 25 °C until the day of testing. The mixes were studied by measuring their 3-, 7-, 28-, 90-, 180- and 360-day compressive strengths with a Toni Technique (Toni Technic, Germany) compressive strength-testing apparatus. For each measurement, 3 specimens were used and the average value was reported as the result. The hardened paste of the mix with 15 % spent catalyst was characterized by laboratory techniques of XRD and SEM. The X-ray diffraction tests were run in a 2 h range of 4-70° at a scanning rate of 2°/min, with a divergence slit of 1°, an anti-scatter slit of 1° and a receiving slit of 0.01 mm. For SEM studies, a number of specimens were cut into halves to expose internal regions. Suitable halves were then coated with gold for SE mode of the microscope. FTIR spectra were collected in transmittance mode from 400 to 4000 cm<sup>-1</sup> using standard KBr technique (0.5 mg sample with 250 mg KBr).

In order to investigate the effect of spent catalyst on the total 90-day shrinkage of the cement paste a number of specimens of  $2 \times 2 \times 10$  cm<sup>3</sup> in size were also prepared and cured for 28 days. After curing, the specimens were stored in an open air atmosphere at a relative humidity of 40 % and a temperature of 25 °C and length changes were measured till the age of 90 days. Water absorption and total permeable open pore volume were also measured according to ASTM C642.

## RESULTS AND DISCUSSION

The mineralogical phase composition of the spent catalyst was determined using powder X-ray diffractometry. Figure 2 shows the X-ray diffraction pattern of the material. As seen, the shape of the pattern and the broad diffuse halo at 2 $\theta$  angle of 23 degrees clearly confirms the presence of amorphous content. The few crystalline mineral phases present in the material are faujasite, quartz, and kaolinite. The mineralogical phase composition of this material is very similar to those reported for FCC spent catalyst [4,5,9,10].

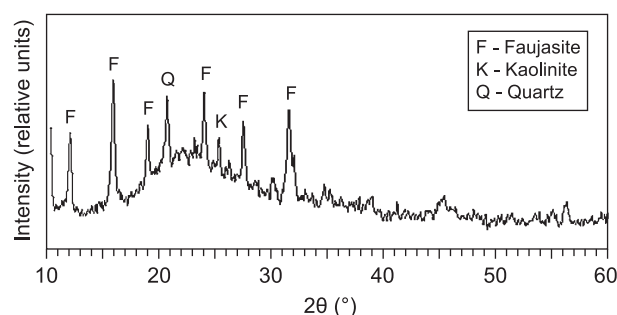


Figure 2. X-ray diffraction pattern of RFCC spent catalyst.

The pozzolanic activity of the spent catalyst was evaluated by measuring the rate of lime combinability in comparison with microsilica and metakaolin as reference pozzolanic materials. Microsilica was chosen as the strongest pozzolanic material. Since the chemical composition of the catalyst is almost similar to metakaolin, and knowing that metakaolin has a high pozzolanic activity, the latter was also used for a better comparison. The pozzolanic activity of the materials was investigated based on thermogravimetric analysis of cured pastes prepared from binary mixes of lime-spent catalyst, lime-microsilica, and lime-metakaolin. The results obtained are presented in Table 2. A comparison of the results clearly shows that spent catalyst is quite a good pozzolanic material exhibiting a rate of lime combinability even faster than metakaolin.

Table 2. Results of thermogravimetric analysis for the amount of reacted calcium hydroxide.

Sample	Reacted $Ca(OH)_2$ (wt.% of pozzolanic material)				
	1 day	3 days	7 days	14 days	28 days
Microsilica	84.46	97.57	100	–	–
RFCC spent catalyst	–	66.82	–	69.14	70.28
Metakaolin	–	48.29	–	53.30	57.46

The pozzolanic activity of the spent catalyst can also be confirmed by FTIR studies. Figure 3 shows the FTIR spectra obtained from samples of lime/spent

catalyst (1:1) after 7 and 28 days of curing. The more relevant peaks include:

- 3640  $\text{cm}^{-1}$  for  $-\text{OH}$  of calcium hydroxide,
- 1366-1417  $\text{cm}^{-1}$  for carbonates (as lime impurities),
- 1100  $\text{cm}^{-1}$  for vibrations of valence  $\text{Si}-\text{O}(\text{Al})-\text{O}$ ,
- 970  $\text{cm}^{-1}$  for calcium silicate hydrates,
- 420  $\text{cm}^{-1}$  for calcium aluminate and calcium aluminosilicate hydrates

It is seen that peaks (a) and (c) belonging to lime and pozzolanic material respectively both decrease while peak (d) belonging to calcium silicate hydrates increases as a consequence of the pozzolanic reaction.

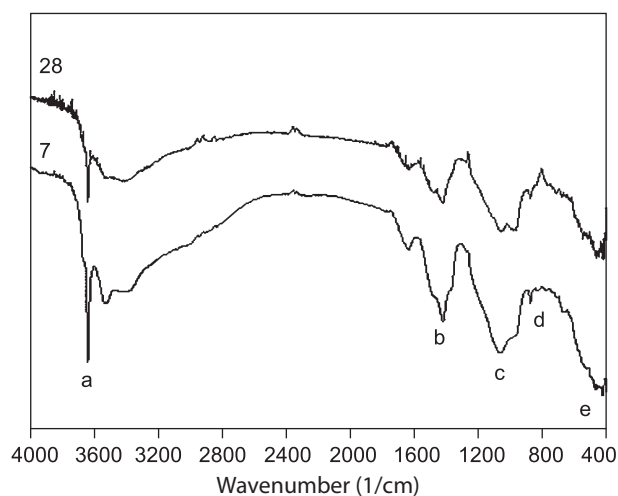


Figure 3. FTIR spectra of lime/spent catalyst (1:1) after 7 and 28 days of curing.

The flow property of the pastes was evaluated by measuring their spread diameter on flow table as a measure of relative workability. Figure 4 shows the effect of spent catalyst on the spread diameter of the pastes. Pastes with better workability would exhibit greater spread diameter. As seen in general, the spread diameter value decreases with increasing the content of catalyst. This is to be attributed to the high specific surface area possessed by the catalyst that provides a great affinity for water absorption. The more the catalyst incorporated, the less the workability of the resulting paste.

Figure 5 shows the effect of spent catalyst on the initial and final setting times of cement paste. Experimental results show that initial and final setting times of Portland cement paste are significantly influenced by the presence of spent catalyst. Generally, the more the cement substitution by the spent catalyst, the shorter the setting times. This is just due to the highly porous microstructure of the spent catalyst providing a large surface area and hence a high capacity of water absorption and not due to the phenomenon of catalyst flocculation in aqueous suspensions that is to be confirmed later. Such high water absorption can

significantly reduce both initial and final setting times. It is also hypothesized that as in the case of microsilica probably the presence of very small particles of spent catalyst can accelerate cement hydration reactions by providing suitable nucleation centers for hydration products [16,17]. However, the particles of spent catalyst are quite larger compared to those of microsilica and this effect that is significant for ultra-fine particles cannot be the governing factor.

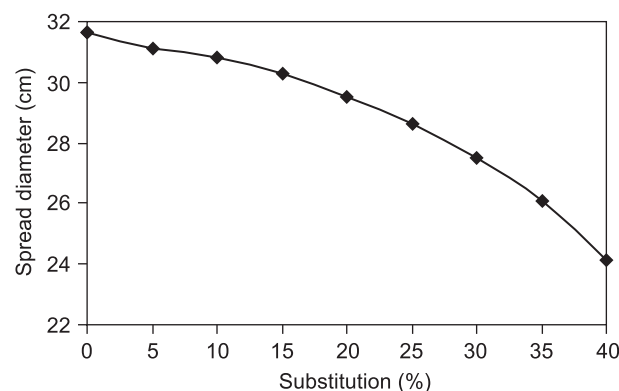


Figure 4. Spread diameter of fresh pastes on flow table.

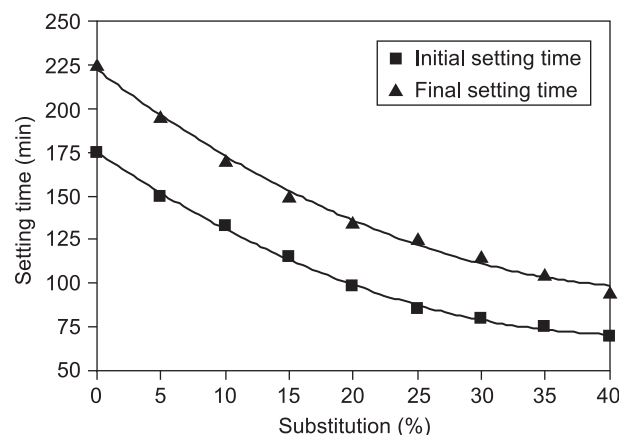


Figure 5. Initial and final setting times of fresh pastes.

Compressive strength of paste specimens prepared at different levels of substitution was also measured after 3, 7, 28, 90, 180, and 360 days of curing. The results obtained are presented in Figure 6. As seen after 3 days of curing, the strength enhancement occurs at replacement level of 5%. By increasing the curing time to 7 days, maximum compressive strength belongs to samples with 10% to 15% substitution and at the age of 28 days, pastes with 15% to 20% replacement show the greatest improvement in compressive strength. These results clearly show that when curing time is short, only a limited amount of calcium hydroxide is released from hydration reactions that could be consumed by a small portion of spent catalyst through the pozzolanic reaction, and most of the catalyst could act just as a porous

microfiller depending on its particle size distribution and its water absorption capacity. It is reported that porous additive materials probably act as internal reservoir in cement paste, providing a more homogenous distribution of large pores feeding the capillary pores or a source of curing water to the paste volume in its vicinity [18]. The result can therefore be an improvement in microstructure development and mechanical strength behavior of the cement paste.

As curing time increases and more calcium hydroxide is produced, more spent catalyst would be required accordingly to achieve sufficient pozzolanic reaction. With higher consumption of calcium hydroxide not only this non-beneficial constituent is removed from the microstructure of the hardened cement paste, but also additional C-S-H gel is produced that in turn results in strength enhancement. As seen, a substitution of cement by spent catalyst between 15% and 20% by weight could increase the 360-day compressive strength of the paste up to 108 MPa that shows 45% increase compared to the plain cement. The enhancement seen in the compressive strength of Portland cement in the presence of RFCC spent catalyst can therefore be attributed to its pozzolanic activity as reported for FCC spent catalyst [4-13].

The positive effect of spent catalyst on compressive strength of Portland cement paste at high substitutions and without dispersing agents confirms the fact that particles of spent catalyst have no tendency to flocculate in aqueous suspensions. This is in contrary to microsilica that has a high tendency to flocculate in aqueous suspensions and requires the use of dispersing agents when utilized as a supplementary cementing material.

X-ray diffraction analyses were carried out on cement pastes containing 0 % and 15 % spent catalyst cured for 90-days in order to study hydration products and to confirm the pozzolanic activity of the material. Figures 7 and 8 show the corresponding X-ray diffraction

patterns. A comparison of the patterns and the few crystalline phases clearly indicates that RFCC spent catalyst exhibits strong pozzolanic activity. The spent catalyst has consumed almost all of the Portlandite. This is in good agreement with results reported by others for FCC spent catalyst [5,6,8].

Figure 9 shows SEM micrographs prepared at different magnifications of 500 and 7500 times from hydrated cement pastes containing 0% and 15% spent

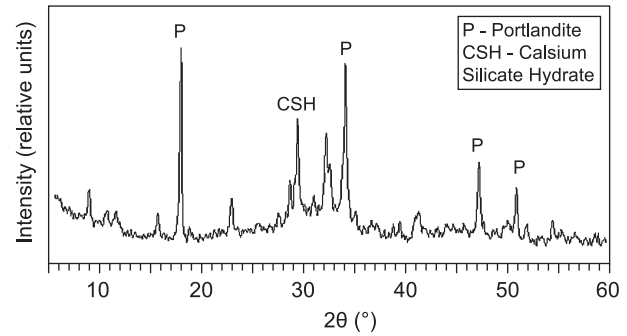


Figure 7. X-ray diffraction pattern of hydrated paste of plain cement after 90 days of curing in water at 25°C.

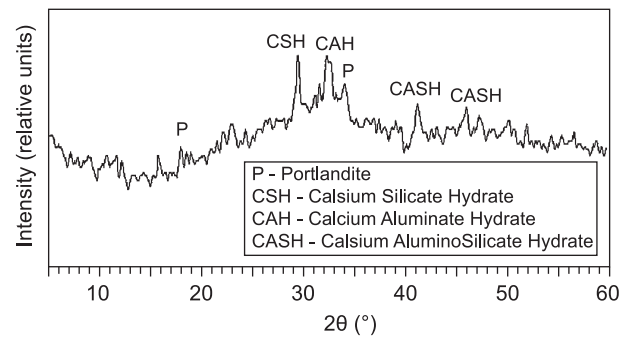


Figure 8. X-ray diffraction pattern of hydrated cement paste with 15 % substitution after 90 days of curing in water at 25°C.

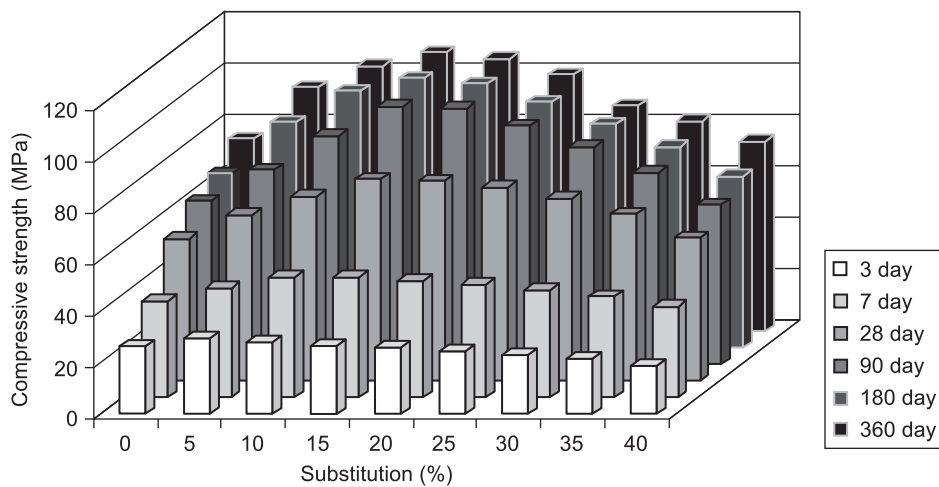


Figure 6. Effect of RFCC spent catalyst on compressive strength of Portland cement

catalyst after 28 days of curing. Careful observations in the case of cement pastes containing spent catalyst revealed a composite microstructure consisting of a matrix in which small particles of different size and shapes are embedded. These embedded particles were relatively large catalyst particles which were not completely reacted and destroyed. Such a partially reacted catalyst particle has been shown in micrograph b). The presence of partially reacted catalyst particles after 28 days of curing shows that relatively larger catalyst particles require longer curing times to effectively take part in the pozzolanic reactions. In spite of the presence of partially reacted catalyst particles, the microstructure of the cement pastes containing spent catalyst appeared to be more uniform considering the content of crystalline constituents. As seen in micrographs c) and d), the microstructure of the cement paste containing spent catalyst showed a significantly lower content of platy and needle-like Portlandite crystals of smaller size. This confirms the effective consumption of Portlandite in pozzolanic reactions which must result in a denser microstructure compared to plain cement paste. Detailed experimental works and suitable laboratory techniques

such as mercury intrusion porosimetry are however necessary to investigate the changes happening in the microstructure and the pore volume of the cement pastes during the course of hydration reactions.

Figure 10 shows the results of shrinkage measurement through 90 days, including both autogenous and drying. The obtained results show that by increasing substitution level up to 10 %, total 90-day shrinkage would decrease and higher substitution percents would

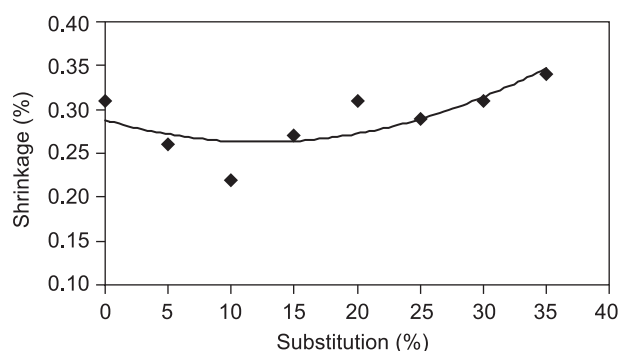
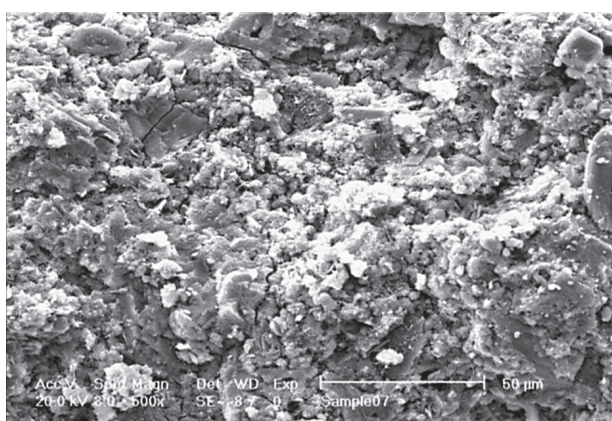
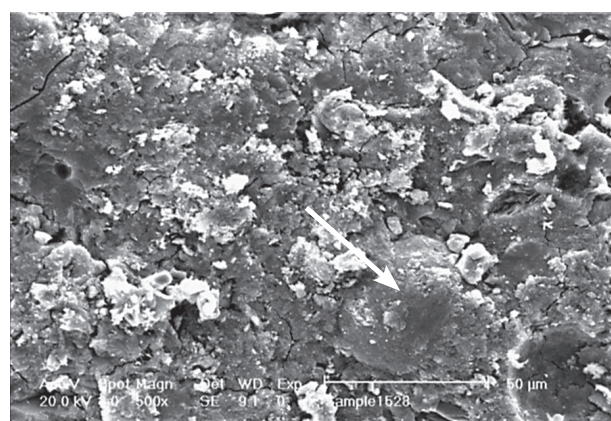


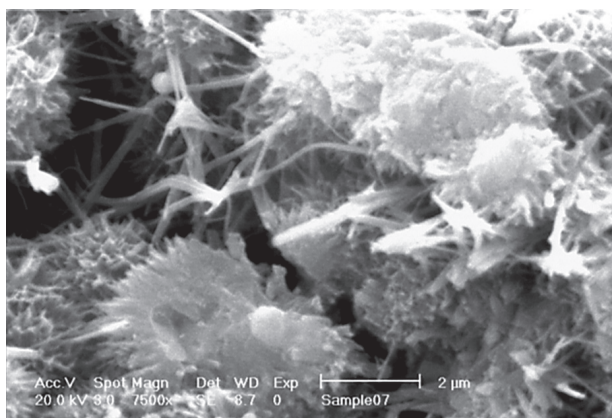
Figure 10. Effect of spent catalyst on total 90-day shrinkage of hardened cement paste.



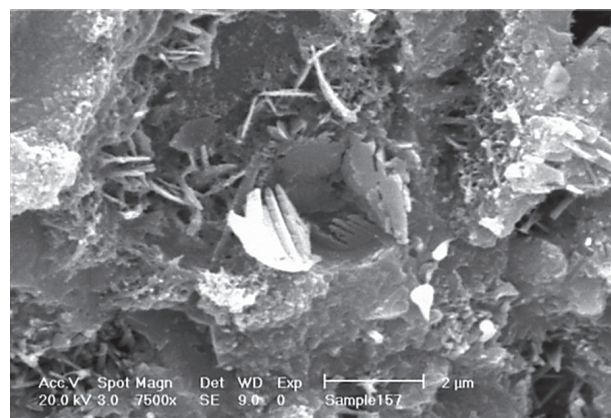
a)



b)



c)



d)

Figure 9. SEM micrographs from microstructure of hardened cement pastes cured for 28 days in water at different magnifications of 500 and 7500 $\times$ , (a,c) plain cement, (b,d) cement containing 15 % spent catalyst.

result in increased shrinkage. It is therefore confirmed that spent catalyst has considerable influence on total shrinkage of Portland cement paste. Interpretation of the results however is not easy, since the observed effects are the overall results of changes brought about in autogenous shrinkage, volume changes due to water absorption, and drying shrinkage. Detailed experimental works are therefore necessary to investigate its individual effects. The positive effect of spent catalyst in reducing total 90-shrinkage at substitutions up to 10 % can probably be attributed not only to its filler effect, but also to its porous microstructure, which affects the distribution of water during hydration [18]. At higher substitution percents, however the effect of pozzolanic reaction on autogenous shrinkage is more pronounced, since chemical shrinkage of the silica reaction is much higher than Portland cement reaction [18]. In addition to pozzolanic reaction, desiccation of physically increased absorbed water by catalyst particles can also result in increased drying shrinkage.

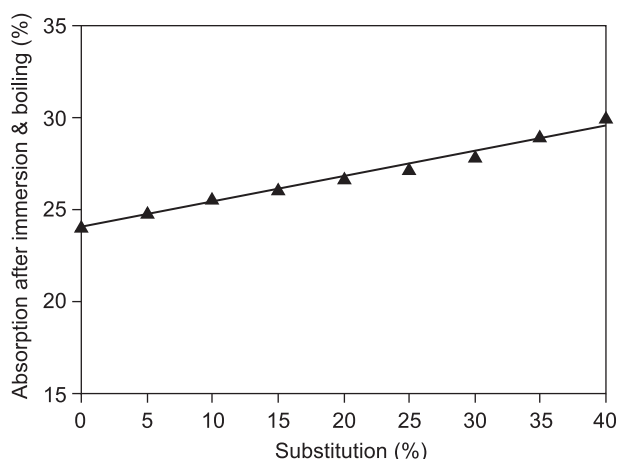


Figure 11. Effect of spent catalyst on water absorption of 28-day cured mortar specimens after immersion and boiling.

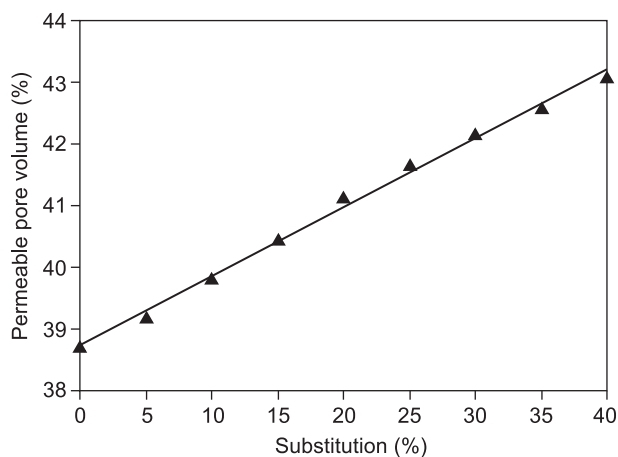


Figure 12. Effect of spent catalyst on total permeable pore volume of 28-day cured mortar specimens.

The results of water absorption and permeable pore volume of the 28-day hardened cement pastes containing spent catalyst along with plain sample are shown in figures 11 and 12. Results clearly reveal that both water absorption and permeable volume increase as cement is replaced by spent catalyst. The higher the substitution percentage, the higher the permeable pore volume and the water absorption. The increase in both permeable pore volume and the amount of water absorption can be attributed to the porous microstructure of the spent catalyst particles. It is important to note that these results are not in contrary to those obtained for compressive strength.

Replacement of cement by spent catalyst from one side acts as an active pozzolanic material effectively consuming calcium hydroxide of the cement paste. The catalyst therefore reduces the microstructural defect points of the hardened cement paste formed by precipitation and accumulation of Portlandite crystals and this means an improvement in the mechanical strength behavior of cement paste. On the other hand, spent catalyst acts as a very fine active and highly porous aggregate that strongly binds to the cement paste and results in an increase in total permeable pore volume. One should however consider the effect of pozzolanic reaction over longer time periods of curing that probably results in lower total permeable pore volume and water absorption compared to the present data. The fineness of the spent catalyst can also probably play an important role on the pore system and permeability of the cement paste. The importance of the permeability of the cement-based materials as a durability determining factor in aggressive environments necessitates detailed experimental work to investigate the effects of spent catalyst on parameters of the pore system and the permeability of the hardened cement paste.

## CONCLUSION

The spent catalyst from Residue Fluidized Catalytic Cracking (RFCC) unit of petroleum refining processes is a very high quality pozzolanic material. According to the results of lime-combinability, this material exhibits the strongest pozzolanic activity after microsilica and behaves better than metakaolin. Utilization of RFCC spent catalyst as a partial replacement of cement strongly affects the basic engineering properties of Portland cement such as paste workability, setting times, and compressive strength. Partial replacement of Portland cement by RFCC spent catalyst decreases the workability and the setting times of the cement paste. A substitution of Portland cement by RFCC spent catalyst between 15 to 20 weight percent of cement could increase the 360-day compressive strength of the paste up to 108 MPa that shows 45 percent increase compared to that of plain Portland cement paste. The interesting result is that high

substitutions even up to 40 weight percent of cement without use of any superplasticizing agent can still result in 28-day compressive strength equal to that of plain Portland cement paste. Replacement of Portland cement by RFCC spent catalyst up to 10 percent by weight of cement reduces total 90-day shrinkage of hardened cement paste. Higher replacement levels however result in increased total 90-day shrinkage. Experimental results obtained from 28-day cured paste specimens show that RFCC spent catalyst, in spite of its significant positive effect on compressive strength, considerably increases both the total open pore volume and the water absorption of hardened Portland cement paste.

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