Cement & Concrete Composites 26 (2004) 657–664

Cement & Concrete Composites

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Spent FCC catalyst as a pozzolanic material for high-performance mortars

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Received 25 September 2001; accepted 27 January 2003

Abstract

Spent fluid catalytic cracking (FCC) catalysts, by-products from oil-cracking refineries, were evaluated as pozzolanic admixtures of concrete. In this study, the activity of two spent FCC catalysts, i.e., Ecat and Epcat, were examined and compared. The pozzolanic activity was indicated by their activity index in presence of Portland cement and the consumption of calcium hydroxide determined by DSC measurements. The effect of these two catalysts on the compressive strength of mortars was also investigated. The results were compared to those of silica fume.

It was found that both Ecat and Epcat, like silica fume, show good pozzolanic activity and are reactive with CH. Furthermore, Epcat possesses much smaller particle size than the other waste catalyst. Therefore, Epcat provides a filling effect on the microstructure and enhances the compressive strength of the resulting mortars. The performance of Epcat is close to or slightly better than that of silica fume. Compared to the control mortar (W/B = 0.42) cured at between 3 and 28 days, mixes with 5–15% cement replacement by Epcat increased the compressive strength by 10–36%.

Keywords: Spent FCC catalyst; Pozzolanic activity; Mortar; Compressive strength

1. Introduction

As the world economy continues to grow and technology to advance, more and more industrial wastes will be produced and the disposal or treatment of these wastes becomes a severe challenge. One possible way to solve this situation is to use wastes as mineral admixtures in concrete. This will not only reduce the consumption of energy in the production of structural materials by partial substitution of cement, but also contribute to environmental protection. Among industrial wastes, silica fume (SF), fly ash, and blast furnace slag are the most successful examples. These materials have cementitious or pozzolanic properties. Their incorporation in concrete not only solves their disposal problems but also improves some properties of concrete. This is because these materials act as microfillers in enhancing the packing at the cement paste–aggregate particle interface and forming a denser and more homogeneous microstructure in the transition zone. Besides, they undergo a pozzolanic reaction with calcium hydroxide (CH) and contribute additional C–S–H gel to the cementitious system and they also accelerate cement hydration. The finer and the more amorphous the pozzolans, the faster their reaction with CH. Therefore, concrete and mortars that incorporate these materials show improved compressive strength and durability [1–4].

In this study, spent fluid catalytic cracking (FCC) catalysts from oil companies were evaluated as mineral admixtures in concrete. These catalysts, mainly composed of silica and alumina, are initially used in FCC units. During the catalytic operation use, part of the catalysts with low activity are removed from the cracking unit and replaced with fresh or regenerated catalysts for maintaining the overall catalytic activity. The removed catalyst is called equilibrium catalyst (Ecat). Separately, some spent catalysts in the form of catalyst fines are generated and collected by an electrostatic precipitator. This waste catalyst is called electrostatic precipitator catalyst (Epcat). Currently, spent FCC

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doi:10.1016/S0958-9465(03)00048-9

catalysts are classified as non-hazardous and the quantity is significant. Furimsky reported that about 400,000 tons were produced annually [5]. Up to now, most of the waste catalysts are solidified and disposed as landfills. However, a potential use of spent FCC catalyst in the area of construction materials such as the filler for asphalt and the production of brick and cement has been suggested [5,6].

Recently, interest in and research on the utilization of spent FCC catalyst as a construction material have been growing. Pacewska et al. [7] have examined the pozzolanic nature of this catalyst using thermal and spectroscopic techniques and have disclosed that its ability to react with CH is similar to microsilica. Paya et al. [8] have demonstrated the high activity of the catalyst previously ground. Su et al. [9,10] and Paya et al. [11] carried out a feasibility study of reusing this waste catalyst and their results indicate that the additive can replace up to 15–20% of cement or 10% of fine aggregate without sacrificing the quality of mortars.

The purpose of this study is to examine and compare the activity of two spent FCC catalysts, i.e., Ecat and Epcat. Mortars containing these two catalysts were prepared and their compressive strengths were measured. To compare the true effect of mineral additives on the compressive strength of the resulting mortars, all tested specimens with or without these inorganic materials present were controlled to have similar workability. This ensured that their microstructures were initially homogeneous with similar packing. The results were also compared to those with silica fume.

2. Experimental

2.1. Materials

The materials used include Type I Portland cement, standard Ottawa sand, a superplasticizer and three mineral additives (Ecat, Epcat and SF). Cement is from the Taiwan Cement Company and complies with ASTM C150. Ottawa sand meets the standard of ASTM C778. The basic properties of cement and additives are listed in Table 1. The superplasticizer used is Raymix, manufactured by the Lignal Company. Raymix is a naphthalene-based superplasticizer (SNF) with 42.7% solids content; it was used to adjust the workability of mortars. Both Ecat and Epcat come from the China Petroleum Corporation. These catalysts consist mainly of SiO_2 and Al_2O_3, and other minute impurities. The average particle size (D_{50}) of Ecat, measured by a Particle Size Analyzer (Coulter LS 230), is 67.2 μm. The BET specific surface area of Ecat, measured by a Surface Area Analyzer (Micromeritics ASAP 2010), is 114 m^2/g. The average particle size and BET specific surface area of Epcat are 1.7 μm and 47.3 m^2/g. Both Ecat and Epcat particles clearly exhibit huge specific surface areas in relation to their particle sizes. Fig. 1 shows the scanning electron micrograph (SEM) of Ecat, indicating that this catalyst indeed has a porous structure. Fig. 2 shows that Epcat has a much smaller particle size with irregular shaped particles. Fig. 3 shows the X-ray diffractogram of an Ecat, indicating that this catalyst is a crystalline material with some amorphous phase in the structure. The crystallized phases been identified include faujasite, quartz, kaolinite, and mullite. Epcat shows a similar X-ray diffractogram as Ecat, except that its crystallized phases are less prominent (Fig. 4). Finally, SF used is a commercially available powder. The high LOI values for Epcat and SF in Table 1 indicate that these materials contain some unburnt carbon.

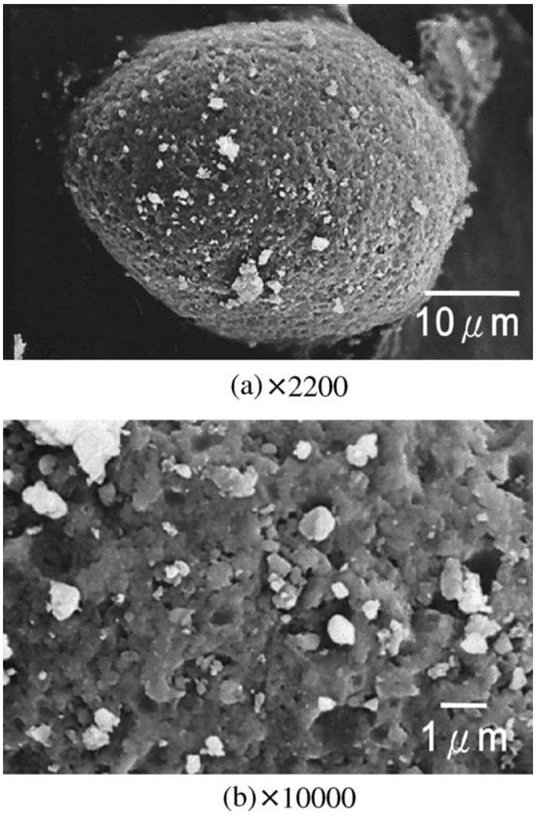
2.2. Preparation of cementitious materials

Pastes were prepared by mixing water, CH and additives (Ecat, Epcat, or SF). The water/(0.5CH + 0.5 additive) ratio was 0.8. The paste samples were sub-

Table 1
Basic properties of cement and additives

	Cement	Ecat	Epcat	SF
Composition (%)				
SiO_2	20.0	50.1	47.0	87.9
Al_2O_3	5.35	38.5	38.0	4.3
Fe_2O_3	3.44	1.37	0.64	0.59
CaO	63.2	–[a]	–	0.32
MgO	2.31	0.71	0.51	–
SO_3	2.03	–	5.6	–
LOI (%)	0.9	1.2	8.9	7.1
Average particle size (μm)[b]	5.2	67.2	1.7	3.8
BET specific surface area (m^2/g)[c]	0.95	114	47.3	12.9
Specific gravity	3.11	2.46	2.38	2.41

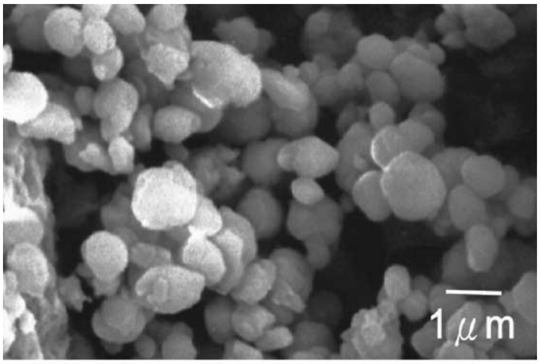
[a] Not measured or trace.
[b] Measured by a Particle Size Analyzer (Coulter LS 230).
[c] Measured by a Surface Area Analyzer (Micromeritics ASAP 2010).



(a) ×2200

(b) ×10000

Fig. 1. SEM of Ecat particles.



×12000

Fig. 2. SEM of Epcat particles.

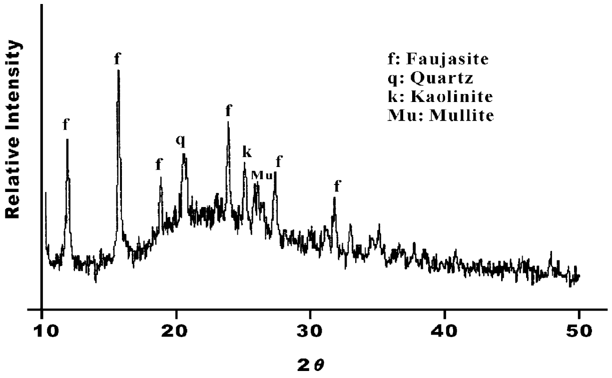


Fig. 3. X-ray diffractogram of an Ecat.

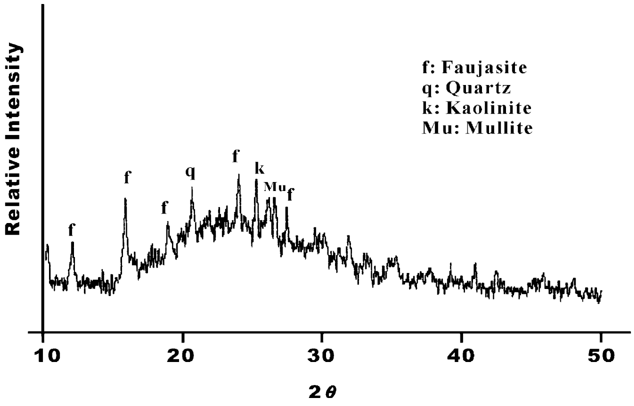


Fig. 4. X-ray diffractogram of an Epcat.

Table 2
Mixture proportions of mortars and AI of mineral additives

	Control	Ecat	Epcat	SF
Cement (g)	250	225	225	225
Sand (g)	687.5	687.5	687.5	687.5
Additive (g)	0	20.6	19.1	17.4
Water (g)	135	145	148	135
Workability (cm)	20.4	20.7	20.1	20.1
Comp. strength (MPa)	31.8	27.4	29.0	29.4
AI		86	91	92

jected to DSC measurements. Mortars were made according to ASTM C230 by mixing water, cement, sand, and with or without addition of additives. Two sets of mortar samples were prepared. The first set was for determining the activity of additives and the mixture proportions are listed in Table 2. The second set was for testing the compressive strength of the resulting mortars. The water/binder (W/B) ratios of this set were 0.42, 0.485 and 0.55; the binder/sand ratio was fixed at 1/2.75. Replacement levels of cement by additives for the mixed mortars were 0, 5, 10, and 15 wt%. The appropriate amount of SNF was added to mortars to obtain similar workability. The mixture proportions are listed in Table 3.

2.3. Activity measurement and testing of mortar mixes

The activity of mineral admixtures was indicated by the activity index (AI) with Portland cement according to ASTM C311. The cement was replaced by each additive in the test mix at a replacement level of 10 vol%. Both control and test mix cubes (5 × 5 × 5 cm), were

Table 3
Mixture proportions, workability and required superplasticizer dosage of mortars for compressive strength measurement

	Control	Ecat	Epcat	SF
Additive/binder (%)	0	5–15	5–15	5–15
W/B = 0.42; sand/binder = 2.75				
SNF/ binder (%)[a]	0.5	0.5–0.7	0.5–0.7	0.5–0.7
Workability (cm)	16–18	16–18	16–18	16–18
W/B = 0.485; sand/binder = 2.75				
SNF/ binder (%)[b]	0.8		1.0–1.2	0.8–1.0
Workability (cm)	19–21		19–21	19–21
W/B = 0.55; sand/binder = 2.75				
SNF/ binder (%)[b]	0.4		0.4–0.6	0.3–0.5
Workability (cm)	19–21		19–21	19–21

[a] SNF/binder (%) is the weight ratio of SNF in a dry state to binder; SNF was added to mixes 3 min after mixing with water.

[b] SNF was added to mixes together with mixing water.

moist cured for 1 day at 23 °C and 6 days at 65 °C, and their compressive strengths measured after 7 days. The AI value is defined as:

$$\mathrm{AI} = 100A/B$$

where A and B are the average compressive strength of the test mix cubes and the average compressive strength of the control mix cubes, respectively.

The workability of mortars was determined and indicated by the spread diameter of tested samples on a flow table according to ASTM C230. Mortar specimens of 5 × 5 × 5 cm were prepared, cured (1 day in a moist plastic bag and then in saturated lime water in a storage tank) at 23 °C and their compressive strengths measured at the ages of 3, 7 and 28 days according to ASTM C109. Each strength value is an average of three measured data.

2.4. Analytical techniques

The microstructure of Ecat or Epcat particles was observed using a scanning electron microscope (JEOL JSM-6300). The mineralogy of waste catalyst was analyzed by a powder X-ray diffractometer (JEOL JDX-8030). The amount of CH of pastes was indicated by an endothermic peak at 450–500 °C measured by a differential scanning calorimeter (Shimadzu TA-50I).

3. Results and discussion

3.1. Activity of mineral admixtures

One method to evaluate the activity of a mineral admixture is to determine the activity index of the inorganic material with Portland cement. In this study, a procedure similar to ASTM C311 was applied, as described in Section 2.3. The mixture proportions of the four mixes, the compressive strength of specimens and the calculated AI value of each additive are listed in Table 2. The Epcat mortar required the greatest amount of water to achieve the required workability with a spread diameter of about 20 cm. Compared to the Epcat mortar, the water requirement is slightly less for the Ecat mortar and much less for the SF mortar or for the control. As mentioned earlier, the catalyst particles show a huge specific area relative to their particle size. For additives such as SF and blast furnace slag, most of the surface area per unit mass derives from their external surface. In contrast, a high proportion of the surface area for both Ecat and Epcat particles is from their internal surface. This will lead to difference in absorption/adsorption characteristics of the catalyst particles, which are likely to be highly absorbent. Therefore, they require more water to achieve similar workability. Table 2 shows that the AI value of Epcat for 10% replacement of cement (91) is close to the value for silica fume (92). Therefore, Epcat should have good activity, for SF is known as a reactive pozzolanic material which not only can induce a rapid pozzolanic reaction, but also contribute a filler effect to the resulting composites [1,12]. In contrast, the AI value of Ecat is 86, which is lower than that of Epcat, mainly because the former has much bigger particle size.

Separately, the pozzolanic activity of each additive was examined by determining the amount of lime consumed with different mineral admixtures along with the time of reaction through DSC measurements. The more of the CH that reacts, the higher is the pozzolanic activity of the mineral admixture. Fig. 5 shows the DSC curves of the pastes with 0.8 water/(0.5CH + 0.5additive) ratio cured at 3 days. The control in Fig. 5 is the paste containing 50% CH and 50% quartz by weight. Generally, the results indicate that all DSC patterns are similar, but the endothermic peak areas are different. The endothermic peak at about 450–500 °C corresponds to

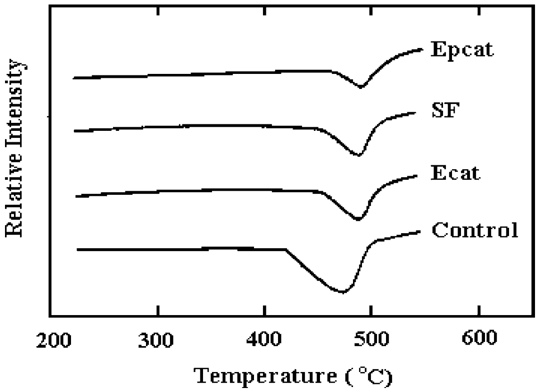


Fig. 5. DSC curves of hydrated pastes cured at 3 days (W/(0.5CH + 0.5additive) = 0.8).

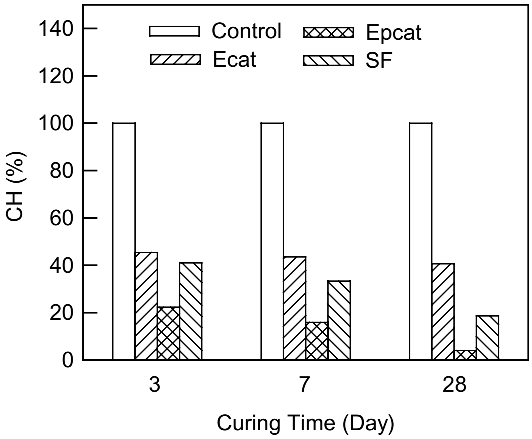


Fig. 6. The percentage of CH of hydrated pastes at different curing times (W/(0.5CH + 0.5additive) = 0.8).

the decomposition of calcium hydroxide to calcium oxide and water [7,13]. A higher peak area indicates greater heat adsorbed or more CH present. The control paste clearly shows the highest endothermic peak area. The peak area decreased when pozzolanic admixtures were incorporated in pastes, indicating that some CH reacted and was consumed by the added pozzolans. Fig. 6 shows the percentage of CH in hydrated pastes at different curing times. The amount of CH in the control paste was defined as 100%. Clearly, all three additives present good pozzolanic activity because more than 50% CH was consumed in each additive-containing hydrated paste at 3 days of curing. As curing time increased, more CH was consumed. The Epcat pastes contain CH 22.3%, 15.9%, and 4.0% less than the control at the ages of 3, 7, and 28 days, respectively. The SF pastes and the Ecat pastes contain CH 41.0–18.6% and 45.4–40.6% less than the control at 3–28 curing ages, respectively. It is apparent that Epcat shows higher pozzolanic activity than the other two.

3.2. Compressive strength of hardened mortars

In order to determine the true effect of mineral admixtures on the compressive strength of the resulting mortars, all tested mortar specimens with or without additives incorporated were designed, as described in Section 1. The required amount of SNF for mortars with Epcat (W/B = 0.485, 0.55) to achieve similar workability is greater than that for mortars with SF (Table 3). As discussed in the previous section, this difference comes from different particle nature of additives. More superplasticizer was required for higher replacement level of additives or lower W/B ratio in mortars to obtain similar workability. However, mortars with W/B = 0.42 shows different results. The SNF dosage added to these mortars is less than those with W/B = 0.485. Besides, the required amount of superplasticizer appears to be a weak function of the type of additives or the additive content. The reason is that SNF was added to these mixes 3 min after mixing with water (delayed addition), not like the other two with higher W/B ratios in which superplasticizer was added together with mixing water. Several results indicate that a delayed addition can reduce the admixture consumption and use less amount of superplasticizer to reach certain workability [1,14].

Figs. 7–9 show the compressive strength of mortars (W/B = 0.42) cured at 3–28 days with 5%, 10% and 15% replacement levels of additives (Epcat, SF, and Ecat), respectively. Again, the workability of all tested mortar samples was almost the same with spread diameter of about 16–18 cm on a flow table. As expected, the compressive strength of mortars with or without additives was found to increase with curing time. Mortars with Epcat or SF show higher strength values than those without. Normally, replacement of cement by mineral

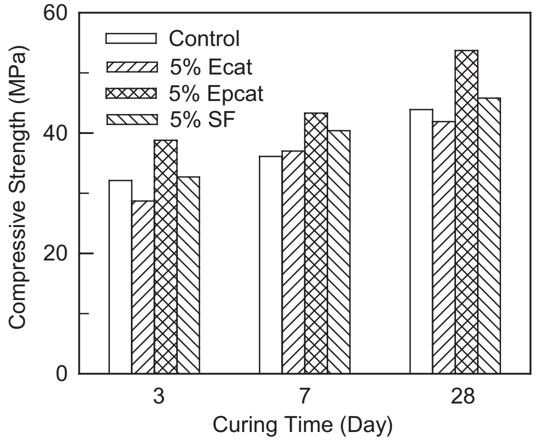


Fig. 7. Compressive strength of mortars with 5% additives (W/B = 0.42).

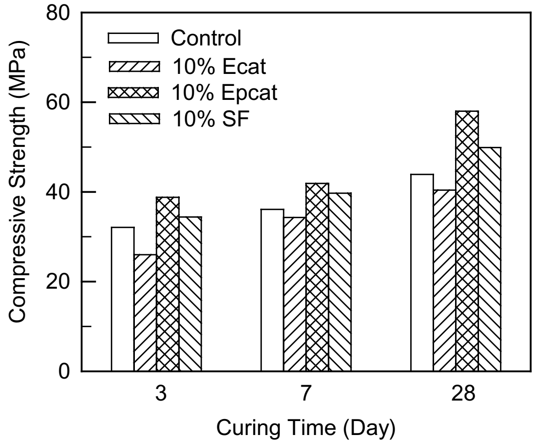


Fig. 8. Compressive strength of mortars with 10% additives (W/B = 0.42).

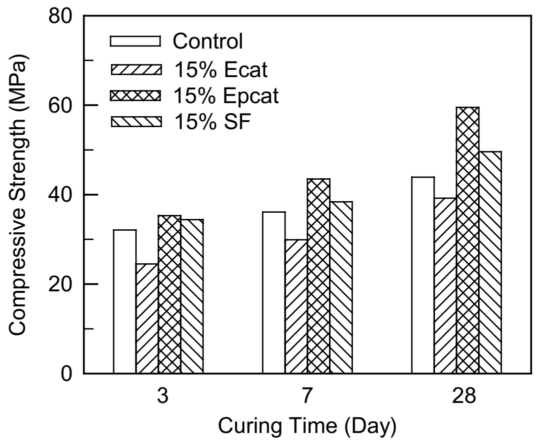


Fig. 9. Compressive strength of mortars with 15% additives (W/B = 0.42).

admixtures would produce a dilution effect and reduce the mechanical properties of the resulting mortars or concrete [2]. However, the compressive strength of materials can be increased if the inorganic fillers are fine enough to enhance the packing of the structure and active enough to increase the rate of cement hydration and generate additional C–S–H gel by pozzolanic reaction, thus enhancing cementation. It is clear that Epcat, like silica fume, belongs to this category of mineral admixture. Such materials exhibit good pozzolanic activity and provide a filling effect so that the compressive strength of the resulting cementitious materials is improved [7,8,12]. Furthermore, the strength improvement is affected by the Epcat replacement level and curing time. At shorter curing time (3 and 7 days), the strength enhancement occurs at replacement level of 5%. At curing time of 28 days, mortars with 15% replacement show the greatest strength improvement. Su et al. have also obtained similar results [9]. When the curing time is short, only a limited amount of CH was released from hydrated cement, which could be consumed by a portion of Epcat through the pozzolanic reaction, and another portion of waste catalyst would act as a microfiller instead of an active pozzolan. Apparently, mortars with 5% Epcat could undergo pozzolanic reaction sufficiently with lime released from cement at 3 days of curing, and show the greatest strength gain. As curing time increased and more CH is produced from hydrated cement, more Epcat would be required accordingly to achieve sufficient pozzolanic reaction and the greatest strength enhancement occurs at a higher replacement level. The Epcat mortars show compressive strengths 10–21%, 16–21%, and 22–36% higher than the control at the ages of 3, 7, and 28 days, respectively. In addition, the strength values of the Epcat mortars are slightly better than those of the SF mortars. In contrast, the compressive strengths of mortars with Ecat were found (Figs. 7–9) to be less than those of mortars without Ecat, indicating that the pozzolanic activity of this waste catalyst is not good enough to overcome the dilution effect within the first 28 days of curing. Nevertheless, the pozzolanic activity of Ecat may contribute to strength development at much later ages. Recently, Huang's study indicates that the Ecat concrete with 10% replacement level cured at between 3 and 28 days has lower compressive strength than the control. However, the compressive strength of the Ecat concrete is higher than that of the control at curing ages between 56 and 91 days [15].

Figs. 10–15 show the compressive strength of mortars cured at 3–28 days with 5–15% replacement levels of additives (Epcat and SF) at higher W/B ratios. As expected, the compressive strength of mortars with or without additives present was found to decrease with increasing W/B. All figures show similar trends as Figs. 7–9; the compressive strength of mortars increases with curing time. Mortars with additives (Epcat or SF) show

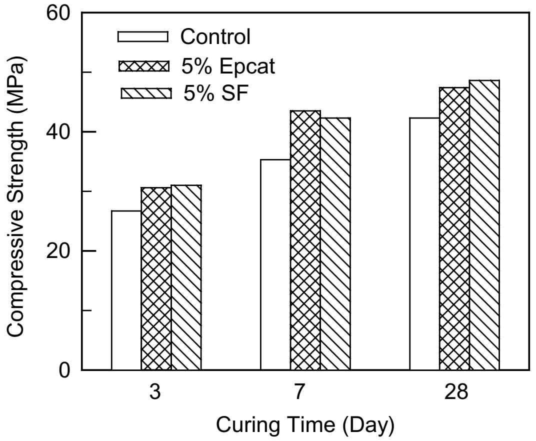


Fig. 10. Compressive strength of mortars with 5% additives (W/B = 0.485).

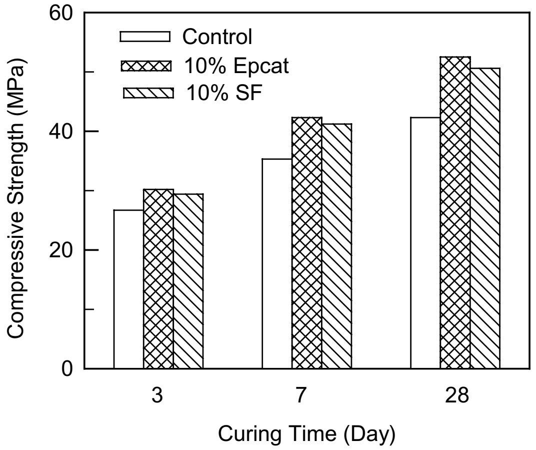


Fig. 11. Compressive strength of mortars with 10% additives (W/B = 0.485).

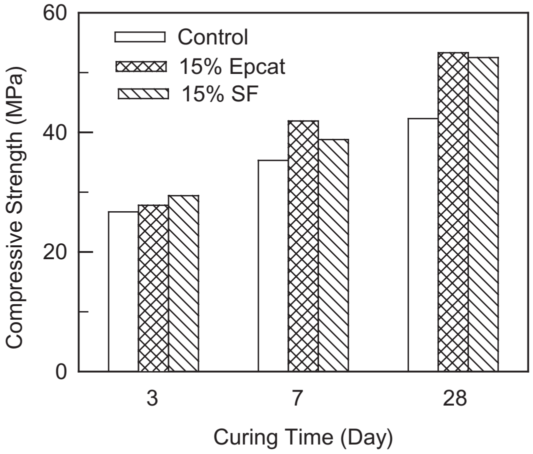


Fig. 12. Compressive strength of mortars with 15% additives (W/B = 0.485).

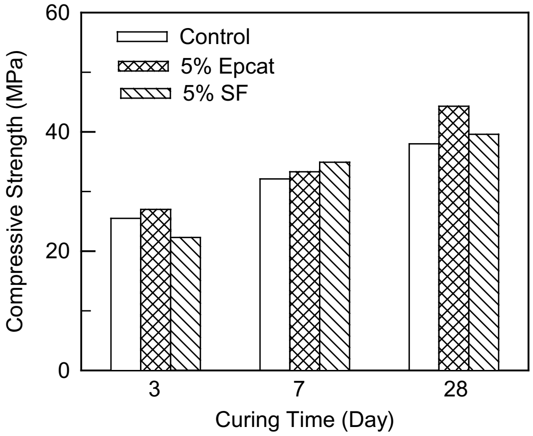


Fig. 13. Compressive strength of mortars with 5% additives (W/B = 0.55).

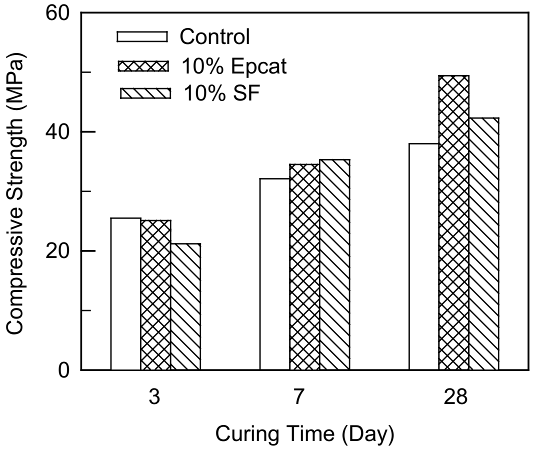


Fig. 14. Compressive strength of mortars with 10% additives (W/B = 0.55).

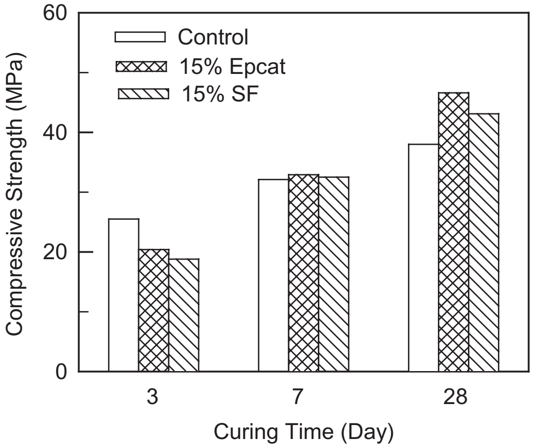


Fig. 15. Compressive strength of mortars with 15% additives (W/B = 0.55).

higher strength values than those without additives. For mortars cured at 3 or 7 days, the compressive strength is the greatest at 5% replacement level and then decreases slightly with Epcat content. For mortars cured at 28 days, the compressive strength increases steadily with Epcat content. Relative to the control mortars, the Epcat mixes with W/B = 0.485 show 10–14%, 17–22%, and 12–26% higher strength values, and those with W/B = 0.55 show −20–6%, 2–8%, and 16–30% higher strength values, at the ages of 3, 7, and 28 days, respectively. Finally, strength values of the Epcat mortars appear to be similar to or slightly better than those of the SF mortars.

4. Conclusions

Both Ecat and Epcat are waste FCC catalysts from oil companies. They were added to mortars as partial replacement of the cement and evaluated as pozzolanic fillers. The results indicate that all three additives show good pozzolanic properties. Epcat, having finer particle size, shows better filling effect and greater pozzolanic activity than another catalyst. It thus provides better strength enhancement than Ecat. The performance of Epcat is close to or slightly better than that of silica fume. A 5–15% cement replacement by Epcat increases the strength of mortars (W/B = 0.42) cured at between 3 and 28 days with respect to the control mortar by between 10 and 36%. Therefore, use of spent FCC catalysts as mineral admixtures in concrete is quite feasible.

Acknowledgements

The authors are grateful for the support extended to this work by the National Science Council of The Republic of China (Contract # NSC-90-2211-E-003-001).

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