Pergamon

Cement and Concrete Research 31 (2001) 1815–1820

CEMENT AND CONCRETE RESEARCH

Oil cracking waste catalyst as an active pozzolanic material for superplasticized mortars

Kung-Chung Hsu[a,*], Yun-Sheng Tseng[a], Fan-Feng Ku[a], Nan Su[b]

[a]Department of Chemistry, National Taiwan Normal University, Taipei 116, Taiwan
[b]Department of Construction Engineering, National Yunlin University of Science and Technology, Yunlin 640, Taiwan

Received 3 January 2001; accepted 25 September 2001

Abstract

Superplasticized mortars containing waste catalyst (EPcat) have been characterized. This waste catalyst comes from catalytic crackers of oil companies. It consists mainly of silicon oxide and aluminum oxide, and shows some amorphous structure. Test results indicate that more superplasticizer or water is required for maintaining the workability of mortars incorporating EPcat. Nevertheless, mortars with EPcat exhibit greater compressive strength than those without. The strength improvement could be attributed to high pozzolanic activity of the waste catalyst. One evidence is that earlier temperature rise was observed in EPcat mortars during hydration than plain ones. Besides, the microstructure analysis indicates that both ettringite and monosulfoaluminate were produced in the early curing period of EPcat mortars. These confirm that EPcat could accelerate the cement hydration by inducing a pozzolanic reaction between the catalyst and calcium hydroxide, the cement hydrated product.

Keywords: Waste catalyst; Pozzolan; Mortar; Workability; Compressive strength

1. Introduction

Mineral admixtures such as silica fume (SF) and metakaolin (MK) are essential supplementary cementing materials for high-performance concrete and mortars. These materials can 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. Most importantly, they can undergo a pozzolanic reaction by reacting with calcium hydroxide (CH) in the cementitious system and accelerate the cement hydration [1–5]. The finer and the more vitreous the pozzolans, the faster is their reaction with CH. Therefore, concrete and mortars incorporated in these materials show improved compressive strength and durability [3,6,7].

In our laboratory, a feasibility study on using a waste catalyst for cement replacement was conducted. The studied catalyst, mainly composed of silica and alumina, is initially used in the fluid catalytic cracking unit (FCCU). After use, part of the catalyst is removed from the cracking unit and refilled with new one for maintaining the overall catalytic activity. The removed catalyst is called equilibrium catalyst (Ecat). Another type of waste catalyst is called electrostatic precipitator catalyst (EPcat), which is the eroded catalyst debris from the cracking unit and is collected by an electrostatic precipitator. The quantity of total waste catalysts produced is significant. The amount of Ecat from the residual oil cracking unit alone is about 6–9 tons/day and that of EPcat accounts for 200–300 kg/day. A report from Furimsky [8] indicated that about 400,000 tons of waste FCCU catalysts were produced annually. Up to now, only a few percentages are made into bricks or ceramic tiles. Most of waste catalysts are solidified and disposed off as landfill [9].

As the oil refining industries continue to grow, the production of waste catalysts is expected to increase. It would be of great value both economically and ecologically if these wastes could be reused. Indeed, this is quite possible. As shown later, these catalysts have similar chemical composition and physical properties as MK [10]. Therefore, they would have pozzolanic activity and could be used as a replacement of cement. In this study, EPcat was

* Corresponding author. Tel.: +886-2-2930-9088; fax: +886-2-2932-4249.

E-mail address: kchsu@cc.ntnu.edu.tw (K.-C. Hsu).

0008-8846/01/$ – see front matter
PII: S0008-8846(01)00693-7

Table 1
Basic properties of cement

SiO_2 (%)	20.04
Al_2O_3 (%)	5.35
Fe_2O_3 (%)	3.44
CaO (%)	63.16
MgO (%)	2.31
SO_3 (%)	2.03
Free CaO (%)	0.99
Ignition loss (%)	0.90
C_3S (%)	48
C_2S (%)	24
C_3A (%)	8.4
C_4AF (%)	10.5
Specific surface area (cm^2/g)	2940
Specific gravity	3.10

used to replace some parts of cement in making mortars. Its effect on the improvement of compressive strength of the resulting mortars was examined and discussed.

2. Experimental

2.1. Materials

The materials used include Type I Portland cement, standard Ottawa sand, a superplasticizer and EPcat. Cement is from Taiwan Cement Corporation and complies with ASTM C150. Ottawa sand meets the standard of ASTM C778. The basic properties of cement are listed in Table 1. A commercial naphthalene-based superplasticizer (SNF) with 42.7% in solid content was used to enhance the workability of tested mortars. EPcat comes from Chinese Petroleum Corporation. The basic properties of EPcat are listed in Table 2. This catalyst is a whitish powder consisting mainly of 50.1 wt.% of SiO_2 and 38.5 wt.% of Al_2O_3, and other minute impurities. It has an average particle size of 1.7 μm, a specific surface area of 47 m^2/g and a specific gravity of 2.36. Fig. 1 shows the scanning electron micrograph (SEM) of EPcat, indicating that this catalyst has irregular shape. Furthermore, an X-ray diffractogram of the catalyst sample shows that EPcat is a crystalline material with some amorphous phase in the structure (see Fig. 2). The crystallized phases that have been identified include SiO_2, Al_2O_3 and mullite. Indeed, its

Table 2
Basic properties of EPcat

SiO_2 (%)	50.1
Al_2O_3 (%)	38.5
Fe_2O_3 (%)	1.37
CaO (%)	–
MgO (%)	0.71
Average particle size (μm)	1.7
Specific surface area (m^2/g)	47
Specific gravity	2.36

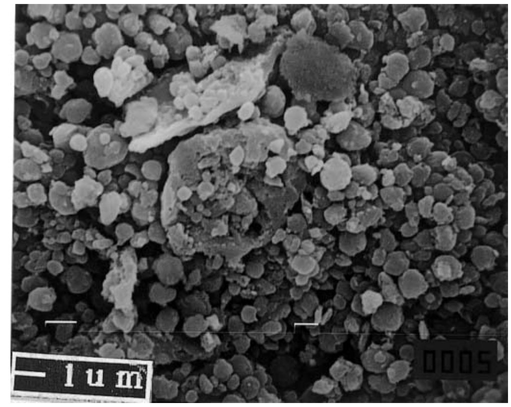


Fig. 1. SEM micrograph of EPcat particles.

chemical composition and physical properties are close to those of MK [10]. Therefore, this catalyst is expected to behave as MK, and can be regarded as an active pozzolan.

2.2. Preparations of cementitious materials

Cement pastes were prepared by mixing water, Type I Portland cement, with or without addition of EPcat. The water/binder (W/B) ratios were 0.485 and 0.8. Mortars were made according to ASTM C230 by mixing water, Type I Portland cement and sand, with or without addition of EPcat. The W/B ratios were 0.485 and 0.55; the binder/sand ratio was fixed at 1/2.75. The superplasticizer/binder (SNF/B) ratios were ranged from 0 to 1.2 wt.%. Replacement levels of cement by EPcat for the mixed cement pastes or mortars were 0, 5, 10, 15 and 30 wt.%.

2.3. Temperature measurement

The temperature variations of cement pastes during hydration were measured and recorded. The temperature of the tested environment was kept at 23 °C and the humidity at 55 RH%.

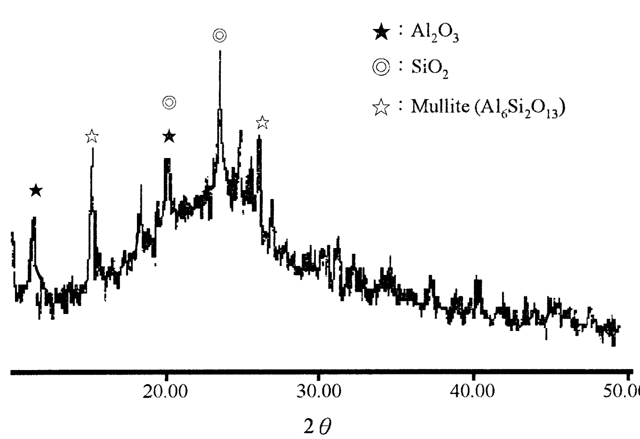


Fig. 2. X-ray diffractogram of EPcat.

2.4. SEM observation

The microstructure of hydrated cement pastes was observed by a scanning electron microscope (JEOL JSM-6300).

2.5. X-ray diffraction (XRD) analysis

The morphologies of EPcat particles or those of hydrated cement pastes were analyzed by a powder X-ray diffractometer (JEOL JDX-8030).

2.6. Workability test

The workability of mortars was determined and indicated by the spread diameter of tested samples on a flow table according to ASTM C230.

2.7. Compressive strength test

Mortar specimens of $5 \times 5 \times 5$ cm were prepared, cured and their compressive strength measured at the ages of 3, 7 and 28 days according to ASTM C348. Each strength value is an average of four measured data.

3. Results and discussion

3.1. Workability of fresh mortars

Before evaluating the oil cracking waste catalyst, i.e., EPcat, on the mechanical properties of mortars, the flow properties and the water demand of the related material were examined. The flow properties of mortars were determined and indicated by the spread diameter of tested samples on a flow table. Fig. 3 shows the effect of replaced EPcat (per unit weight of cement) on the spread diameter of the resulting mortars (W/B = 0.485). Mortars with better workability would exhibit greater spread diameter. In general, the diameter value decreases with replaced EPcat. This is attributed to the high specific surface area possessed by the catalyst, which has great affinity for water. The more the EPcat incorporated, the less the workability of the resulting mortars. Accordingly, greater water demand would be needed in the cementitious system incorporated with more EPcat, while maintaining similar workability. Fig. 4 is the effect of replaced EPcat on the spread diameter of the resulting mortars with higher W/B ratio, i.e., W/B = 0.55. Although the trends in these two figures are almost the same, the required SNF dosage for mortars with higher W/B ratio is much less to achieve similar flowability. For mortars with constant amount of catalyst, the spread diameter will increase with SNF dosage. Clearly, this is because of the improved dispersing effects on cement particles induced by the superplasticizer.

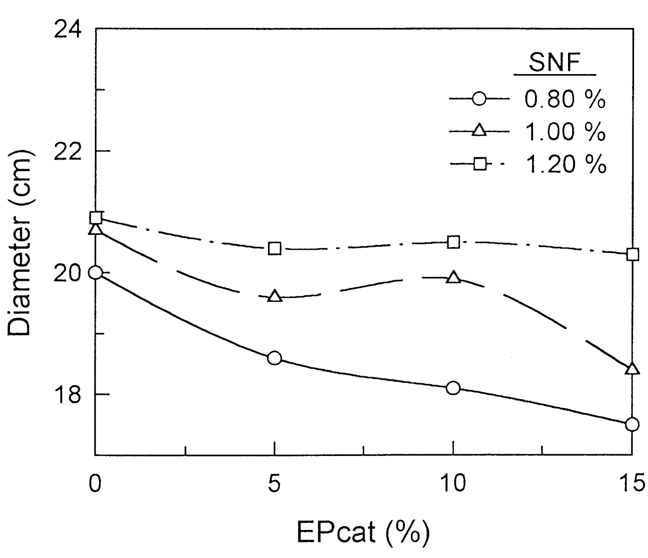


Fig. 3. The effect of EPcat on the workability of mortars (W/B = 0.485).

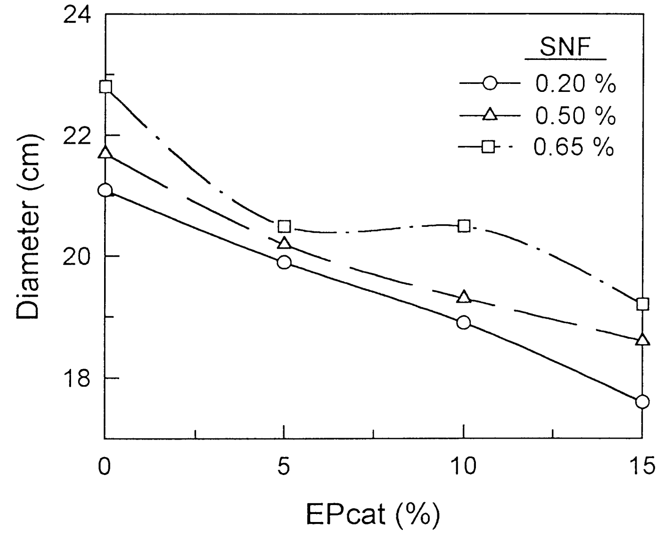


Fig. 4. The effect of EPcat on the workability of mortars (W/B = 0.55).

3.2. Compressive strength of hardened mortars

Fig. 5 shows the effect of EPcat on the compressive strength of mortars (W/B = 0.55) cured at 3, 7 and 28 days. In general, the compressive strength of mortars is increased with time. The workability of EPcat mortars is adjusted to be similar to the control or plain one, i.e., the mortar without catalyst. In other words, the workability of all tested mortar samples was almost the same with spread diameter of about 20 cm. This was achieved by adding proper amount of SNF into each mix. Mortars with the catalyst present higher strength value than those without catalyst. As will be shown later, the strength enhancement by EPcat is due to the acceleration of the cement hydration and the initiation of a pozzolanic reaction. Normally, replacement of cement in mortars or

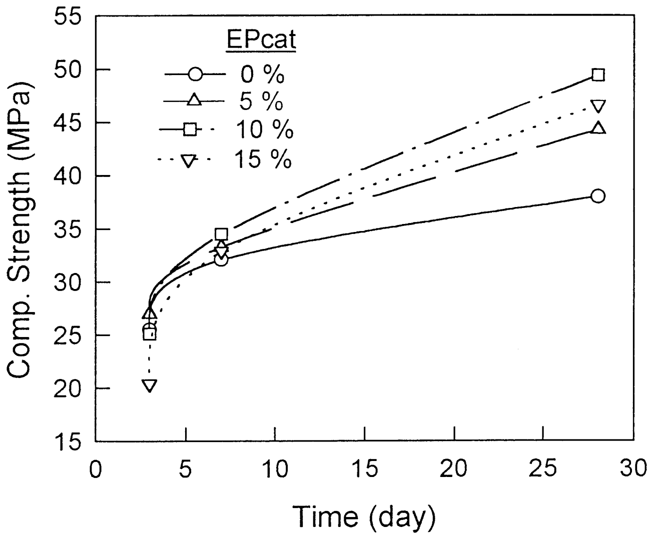


Fig. 5. The effect of EPcat on the compressive strength of mortars (W/B = 0.55).

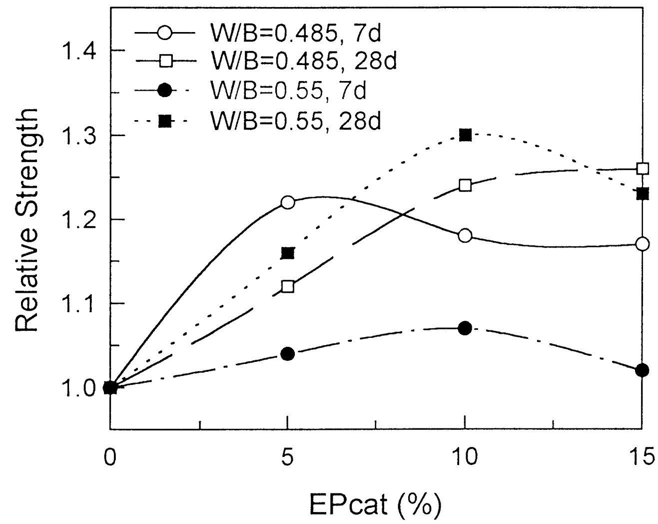


Fig. 6. The effect of EPcat on the relative strength of mortars.

concrete by mineral admixtures would produce a dilution effect and reduce the mechanical properties of the resulting materials [4]. In contrast, the compressive strength of materials would be increased if the inorganic fillers could increase the rate of cement hydration and generate a pozzolanic reaction. EPcat appears to be qualified in this regard [1,3]. For 5% replacement, the compressive strength of mortars is slightly higher than that of the control one. For 10% or 15% replacement, the dilution effect becomes dominant and the EPcat mortars show lower strength values than the plain one. At the age of 3 days, the dilution effect and the contribution of accelerating cement hydration and generating a pozzolanic reaction seem to be compensated with each other. At the age of 7 and 28 days, the contribution of increasing the rate of cement hydration and generating a pozzolanic reaction overcomes the dilution effect. Therefore, mortars with the catalyst show higher strength values.

Fig. 6 shows the relative strength of mortars at different curing ages and two W/B ratios. The relative strength is defined as the ratio of the compressive strength of EPcat mortars to that of plain ones. It is seen that the relative strength is increased with curing time, as the contribution by the pozzolanic reaction becomes more significant. The improvement of mechanical property is considered to be prominent if the relative strength value is greater than 1.1. For mortars with W/B = 0.55, the strength enhancement by the catalyst becomes prominent only at 28 days cured age. For mortars with lower W/B ratio (W/B = 0.485), this effect starts earlier, namely at the age of 7 days. Besides, a 10–15% cement replacement by EPcat increases the compressive strength of mortars at 7–28 days, with respect to the control one, of about 20–30%; that is close to the results achieved by either MK or SF [4,10,11].

3.3. Temperature profile of cement pastes

Measuring the rate of temperature variation during the hydration of cement is a method to examine the effect of EPcat on the cement hydration. Fig. 7 shows the temperature profile of cement pastes (W/B = 0.485) containing 0%, 5%, 10% and 15% catalyst with curing time. As expected, two exothermal peaks were observed. Addition of EPcat modifies the temperature profile of the curves, especially the second peak. The first peak below 1 h is attributed to the C_3A hydration, while the second one at about 6–7 h is caused by the C_3S hydration. For cement pastes containing the catalyst, the corresponding second peaks occur earlier,

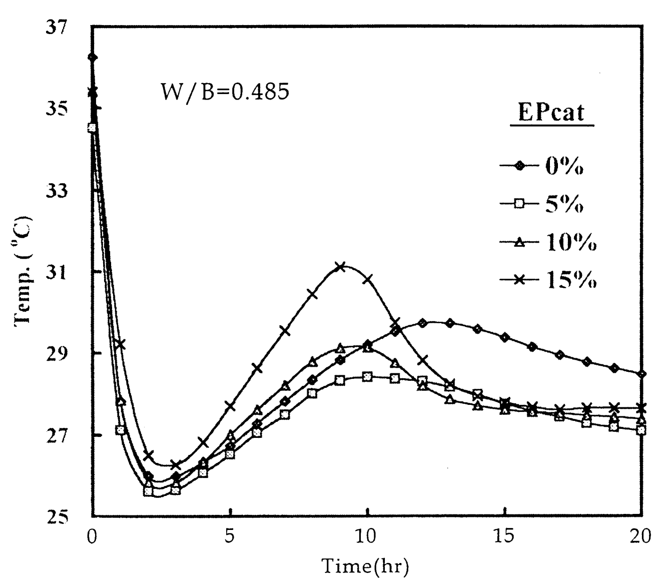
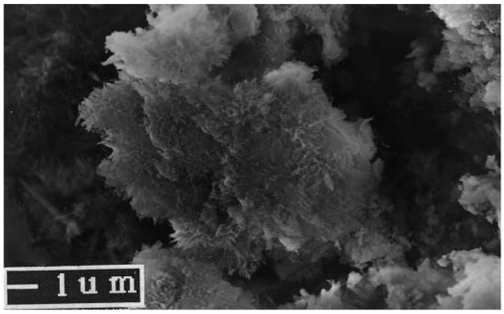
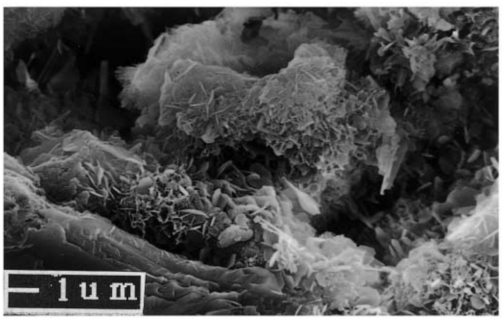


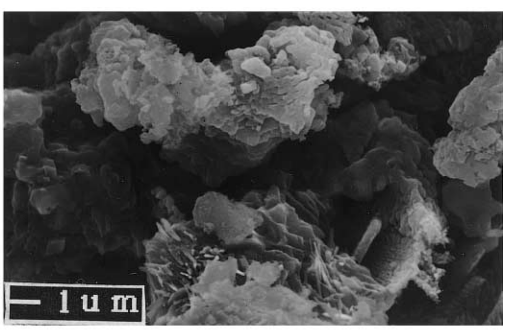
Fig. 7. The effect of EPcat on the temperature rise of cement pastes (W/B = 0.485).



(a) 3 days



(b) 7 days



(c) 28 days

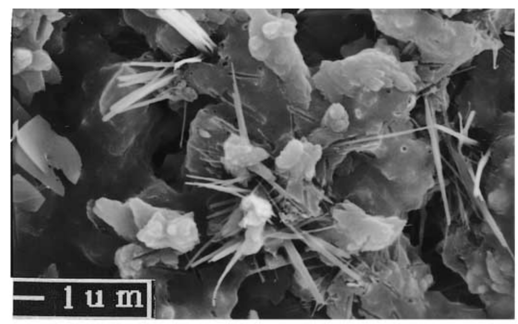
Fig. 8. SEM micrographs of hydrated cement pastes without EPcat (W/B = 0.8).

and the intensities of these peaks are greater. As the amount of added catalyst increases, the occurrence of the second peak is shortened and the intensity is increased. For mortars with 15% cement replacement, the intensity of the second peak is even higher than that of the control one. Similar results have also been reported for cement pastes incorporated with either SF of MK. This confirms that EPcat, like SF or MK, could accelerate the cement hydration.

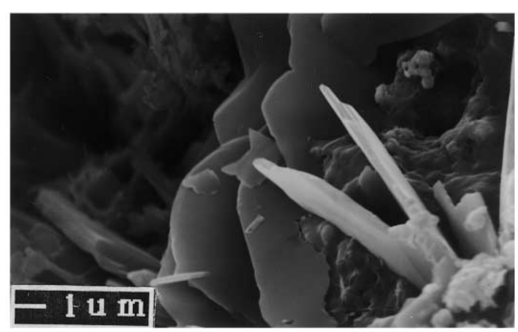
3.4. Microstructure of cement pastes

Fig. 8 shows SEM micrographs of hydrated cement pastes (W/B = 0.8) at different ages without the presence of EPcat. Regardless of the hydrated time, a spiny appearance representing the amorphous C–S–H structure was clearly seen in these micrographs. Besides, some pores or voids were also observed. When the waste catalyst was added, the microstructure of hydrated cement pastes is clearly different from the previous one. Fig. 9 shows SEM micrographs of hydrated cement pastes (W/B = 0.8) at different ages with the presence of 30% EPcat. At the age of 3 days, a few of long slender needles were observed in Fig. 9a, indicating the formation of Ettringite (AFt). When the hydration time increases, monosulfoaluminate (AFm) with a platy, hexagonal shape appears [12]. At the age of 28 days, both AFt and AFm phases could be found.

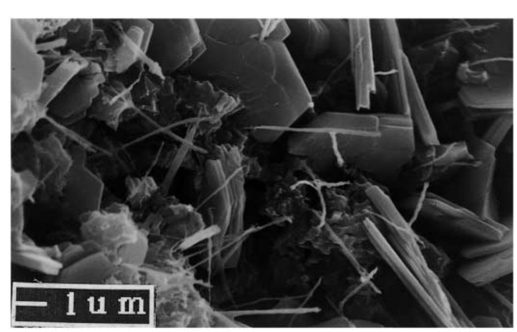
Separately, Fig. 10 shows XRD patterns of hydrated cement pastes containing 30% EPcat (W/B = 0.8) cured at 3, 7 and 28 days. Generally, the results indicate that all patterns are similar, but the intensity of hydration pro-



(a) 3 days



(b) 7 days



(c) 28 days

Fig. 9. SEM micrographs of hydrated cement pastes with EPcat (W/B = 0.8).

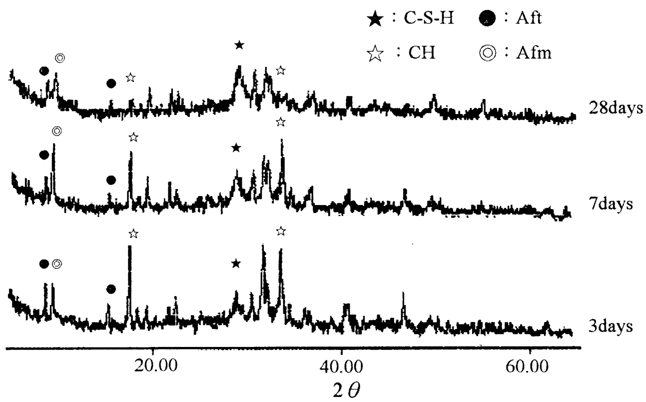


Fig. 10. XRD patterns of hydrated cement pastes with EPcat (W/B = 0.8).

ducts, especially CH and C–S–H, is different. It is clear that the intensity of CSH ($2\theta = 29°$) increases but that of CH ($2\theta = 18°$) decreases with the hydrated time. This provides another evidence that incorporating EPcat into cement pastes would induce the pozzolanic reaction by consuming CH. Besides, other hydrated product, i.e., Aft ($2\theta = 9.1°$) and Afm ($2\theta = 9.9°$), were also found for the pastes at different ages [13].

4. Conclusions

EPcat is the waste catalyst from oil companies. It was added into mortars and evaluated as a pozzolanic filler for the replacement of cement. The tested results present that this catalyst could increase the compressive strength of mortars. A 10–15% cement replacement by EPcat increases the strength of mortars at 7–28 days, with respect to the control one, of about 20–30%. This performance is close to that by either MK or SF. The strength improvement is attributed to high pozzolanic activity of the catalyst, as shown by the temperature profile as well as microstructure analyses of cement pastes with EPcat.

Acknowledgments

The authors are grateful for the support of this work by the National Science Council of The Republic of China (contract no. NSC 90-2211-E-003-001).

References

[1] M.I.S. de Rojas, M. Frías, The pozzolanic activity of different materials, its influence on the hydration heat in mortars, Cem. Concr. Res. 26 (2) (1996) 203–213.
[2] A.A. Al-Manaseer, L.D. Keil, Physical properties of cement grout containing silica fume and superplasticizer, ACI Mater. J. 89 (2) (1992) 154–160.
[3] S. Wild, B.B. Sabir, J.M. Khatib, Factors influencing strength development of concrete containing silica fume, Cem. Concr. Res. 25 (7) (1995) 1567–1580.
[4] S. Wild, J.M. Khatib, A. Jones, Relative strength, pozzolanic activity and cement hydration in superplasticised metakaolin concrete, Cem. Concr. Res. 26 (10) (1996) 1537–1544.
[5] D.R.G. Mitchell, I. Hinczak, R.A. Day, Interaction of silica fume with calcium hydroxide solutions and hydrated cement pastes, Cem. Concr. Res. 28 (11) (1998) 1571–1584.
[6] H.A. Toutanji, T. El-Korchi, The influence of silica fume on the compressive strength of cement paste and mortar, Cem. Concr. Res. 25 (7) (1995) 1591–1602.
[7] M.D. Cohen, A. Bentur, Durability of Portland cement–silica fume pastes in magnesium sulfate and sodium sulfate solutions, ACI Mater. J. 85 (3) (1988) 148–157.
[8] E. Furimsky, Spent refinery catalysts: environment, safety and utilization, Catal. Today 30 (4) (1996) 223–286.
[9] W.C. Hsu, Utilization of the ceramic products made from wastes, Ceramics 15 (1) (1996) 20–35.
[10] M.H. Zhang, V.M. Malhotra, Characteristics of a thermally activated alumino-silicate pozzolanic material and its use in concrete, Cem. Concr. Res. 25 (8) (1995) 1713–1725.
[11] F. Curcio, B.A. DeAngelis, S. Pagliolico, Metakaolin as a pozzolanic microfiller for high-performance mortars, Cem. Concr. Res. 28 (6) (1998) 803–809.
[12] S. Mindess, J.F. Young, Concrete, Prentice-Hall, New Jersey, 1981.
[13] B.A. Clark, P.W. Brown, The formation of calcium sulfoaluminate hydrate compounds, Part II, Cem. Concr. Res. 30 (2) (2000) 233–240.