Available online at www.sciencedirect.com
SCIENCE DIRECT
Cement and Concrete Research 35 (2005) 782–787
CEMENT AND CONCRETE RESEARCH

The pozzolanic activity of a calcined waste FCC catalyst and its effect on the compressive strength of cementitious materials

Yun-Sheng Tseng, Chen-Lin Huang, Kung-Chung Hsu*

Department of Chemistry, National Taiwan Normal University, Taipei 116, Taiwan, ROC

Received 10 October 2003; accepted 19 April 2004

Abstract

Equilibrium catalyst (Ecat), one of the spent fluid catalytic cracking (FCC) catalysts from oil companies, shows pozzolanic activity. In this study, the effects on the pozzolanic activity of calcination of Ecat and on the compressive strength of the resulting cementitious materials were examined. The pozzolanic activity of this mineral additive was indicated from DSC measurements. The results show that the pozzolanic activity of Ecat increases with calcined temperature initially, reaches a maximum, and then decreases afterwards. Ecat calcined at about 650 °C becomes the most active. Mortars with 10% calcined catalyst at 3–28 curing days exhibit strength 8–18% greater than that with the untreated. Concrete with a 10% calcined Ecat at 3–28 curing days exhibits strength 7–11% greater than that with the untreated. If the calcined catalyst is further ground, its pozzolanic activity is enhanced, and the compressive strength of the resulting mortars or concrete becomes higher.

Keywords: Waste catalyst; Calcination; Grinding; Pozzolanic activity; 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 release this situation is to use them as mineral admixtures in concrete. Economically, it will reduce the cost and consumption of energy in the production of structural materials by partial substitution of cement. Environmentally, the disposal problems of these wastes can be solved, and CO_2 emission during cement manufacture is reduced. Besides, the incorporation of them in concrete will also improve engineering properties such as compressive strength and durability of the resulting material [1–4].

Among the industrial wastes, silica fume, fly ash, and slag are the successful examples. The prerequisite of using these wastes as concrete admixtures is that they should have cementitious or pozzolanic properties. Recently, spent fluid catalytic cracking (FCC) catalysts from oil companies have also been considered as potential concrete additives because they are mainly composed of silica and alumina and exhibit pozzolanic activity [5–9]. Some articles indicate that these spent catalysts can partially replace cement or fine aggregate without sacrificing the quality of cementitious materials [10–17].

During the catalytic operation in FCC units, two kinds of waste catalysts are generated. One is called electrostatic precipitator catalyst (Epcat), and another is called equilibrium catalyst (Ecat). Although both catalysts show pozzolanic activity, Chen et al. [17] indicate that a 5–15% cement replacement by Epcat could greatly improve the compressive strength of mortars cured at 3–28 days. In contrast, the compressive strength of mortars with Ecat is generally less than that without this catalyst. It is noted that the amount of Ecat generated annually is much more than that of Epcat. Therefore, it is worthwhile to enhance the pozzolanic activity of Ecat and promote its utilization as construction material.

Separately, it is well known that the pozzolanic activity of clays can be improved greatly by proper thermal treatment. For example, sepiolite, after being calcined at 830 °C, becomes an active pozzolanic material and can increase the compressive strength of the resulting mortar to 84% of that the reference mortar [18]. Metakaolin is a pozzolanic material obtained by calcination of kaoline clay at a tem-

* 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/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2004.04.026

perature of between 650 and 850 °C [19–21]. Sabir et al. [22] have reviewed its use as partial cement replacement for mortars and concrete.

As the chemical composition of Ecat is close to that of metakaolin; the pozzolanic activity of the waste catalyst is expected to increase if it was calcined properly. In this study, the effect of Ecat treated thermally at different temperatures on the enhancement the pozzolanic activity was examined, and the compressive strength of the resulting cementitious materials were measured and discussed.

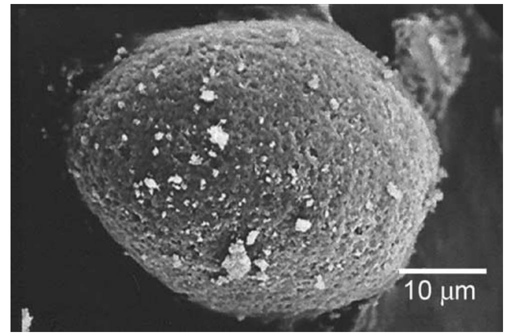

Fig. 1. SEM of Ecat.

2. Experimental

2.1. Materials

The materials used include Type I Portland cement, standard Ottawa sand, river gravel (from Midwest Taiwan), a superplasticizer, and an additive (Ecat). Cement is from Taiwan Cement and complies with ASTM C150. Both sand and stone meet the standard of ASTM C33. The basic properties of cement and additive are listed in Table 1. The superplasticizer used is Raymix, manufactured by Lignal. Raymix is a naphthalene-based superplasticizer (SNF) with 42.7% solids content; it was used to adjust the workability of both mortars and concrete. Ecat comes from China Petroleum and is composed mainly of SiO_2 and Al_2O_3. The average particle size and specific surface area of Ecat are 67.2 μm and 114 m^2/g, respectively. Fig. 1 shows the scanning electron micrograph (SEM) of Ecat, indicating that this catalyst indeed has a porous structure. Fig. 2 shows the X-ray diffraction (XRD) diagram of an Ecat, indicating that this catalyst is a crystalline material with some amorphous phase in the structure. The crystallized phase been identified is mainly Faujasite (sodium aluminate silicate hydrate).

2.2. Treatment of waste catalyst

The calcination of Ecat was carried out in a laboratory oven. The appropriate amount of the catalyst was put in alumina crucibles and thermally treated in the oven at a heating rate of 10 °C/min from room temperature to 450, 650, 750, 850, 950, 1000, 1050, and 1100 °C, where it remained for 1 h. The calcined Ecat was then removed out of the oven and quenched in water to room temperature. Besides, some heat-treated catalyst was further ball milled for 2 h and the particle size was reduced to 3.2 μm.

2.3. Preparation of cementitious materials

Pastes were prepared by mixing water, CH, and additives (the raw Ecat and the treated). The water/(0.9 CH + 0.1 additive) ratio was 0.8. The paste samples were subjected to DSC measurements to determine their amount of CH. Both mortars and concrete were made according to ASTM C387 by mixing water, cement, sand, and/or stone, and with or without the addition of additives. The appropriate amount of SNF was added to both mortars and concrete to obtain similar workability. 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) ratio of this set was 0.42; the binder/sand ratio was fixed at 1:2.75. The replacement levels of cement by additives for the mixed mortars were 0 and 10 wt.%. The mixture proportions of the concrete are listed in Table 3, and the compressive strength was measured.

Table 1
Basic properties of cement and additive

	Cement	Ecat
Composition (%)		
SiO_2	20.0	50.1
Al_2O_3	5.35	38.5
Fe_2O_3	3.44	1.37
CaO	63.2	–[a]
MgO	2.31	0.71
SO_3	2.03	–
LOI (%)	0.9	1.2
Average particle size (μm)	14.3	67.2
BET specific surface area (m^2/g)	1.09	114
Specific gravity	3.11	2.46

[a] Not measured or trace.

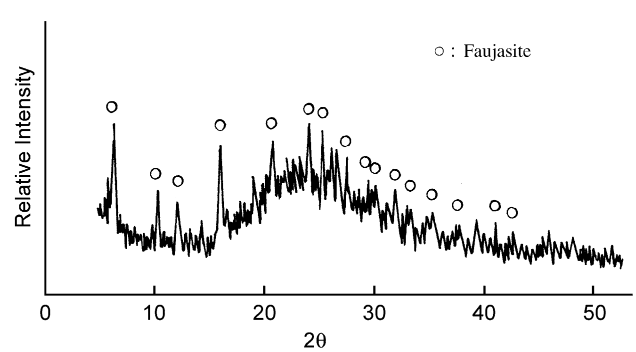

Fig. 2. XRD diagram of Ecat.

Table 2
Mixture proportions of mortars and AI of mineral additives

	Control	m0[a]	m1[b]	m2[c]
Cement (g)	250	225	225	225
Sand (g)	687.5	687.5	687.5	687.5
Additive (g)	0	20.6	20.6	20.6
Water (g)	135	145	145	145
Workability (cm)	20.4	20.7	21.2	20.3
7-Day compressive strength (MPa)	32.9	28.3	29.1	29.9
AI		86.0	88.4	90.8

[a] Mortars with raw Ecat.
[b] Mortars with treated Ecat (650 °C, 1 h).
[c] Mortars with treated Ecat (650 °C, 1 h; grinding, 2 h).

2.4. Pozzolanic activity of additives and testing of cementitious mixes

The pozzolanic activity of additives was shown by (1) the amount of CH consumed in pastes along with reaction time, which was indicated by the difference of an endothermic peak area at 450–500 °C, measured by a differential scanning calorimeter (Shimadzu TA-50I) and (2) the activity index (AI) with Portland cement according to ASTM C311, with some modifications. Namely, the cement was replaced by additive in the test mix at a replacement level of 10 vol.%. Both the control and test mix cubes ($5 \times 5 \times 5$ cm) were moist cured for 1 day at 23 °C and for 6 days at 65 °C, and their compressive strengths measured after 7 days. The AI value is defined as

$$AI = 100A/B$$

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 $5 \times 5 \times 5$ cm were prepared and cured, and their compressive strengths were measured at the ages of 3, 7 and 28 days according to ASTM C109.

Table 3
Mixture proportions and compressive strengths of 1 m^3 concrete

		Control	C0[a]	C1[b]	C2[c]
Cement (kg)		424	381.6	381.6	381.6
Sand (kg)		961	961	961	961
Stone (kg)		743	743	743	743
Additive (kg)		0	42.4	42.4	42.4
Water (kg)		178.1	178.1	178.1	178.1
SNF (kg)		6.36	6.36	6.36	6.78
Slump (cm)		25	25.7	25.2	25.7
Compressive	3 day	37.4	33.1	35.3	36.9
strength	7 day	48.0	45.2	50.2	52.4
(MPa)	28 day	50.6	50.0	53.4	54.2

[a] Concrete with raw Ecat.
[b] Concrete with treated Ecat (650 °C, 1 h).
[c] Concrete with treated Ecat (650 °C, 1 h; grinding, 2 h).

The workability of concrete was determined and indicated by the slump value of tested samples on a slump cone according to ASTM C143. Concrete samples of $10\varphi \times 20$ cm were prepared, cured, and their compressive strengths measured at the ages of 3, 7 and 28 days according to ASTM C39. Each strength value of the cementitious material is an average of three measured data.

2.5. Analytical techniques

The microstructure of the Ecat 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 particle size of the additive was measured by a Particle Size Analyzer (Coulter LS 230), and the specific surface area measured by a Surface Area Analyzer (Micromeritics ASAP 2010).

3. Results and discussion

The pozzolanic activity of mineral admixtures can be determined from the change of the amount of CH consumed in pastes containing these additives along with reaction time, which was indicated by DSC measurements. The more the CH has been reacted, the higher the pozzolanic activity of the mineral admixture. Fig. 3 shows the DSC curves of the pastes with 0.8 water/(0.9 CH + 0.1 additive) ratio cured at 7 days. The endothermic peak at about 450–500 °C corresponds to the decomposition of calcium hydroxide to calcium oxide and water [8,23]. The control, which is the paste containing 90% CH and 10% quartz by weight, clearly shows a larger endothermic peak area. The peak area becomes decreased when Ecat was incorporated in pastes, indicating that some CH been consumed and the added catalyst have certain pozzolanic activity. The peak area is reduced further if the added Ecat undergone calcination at 450 °C for 1 h. Fig. 4 shows the effect of

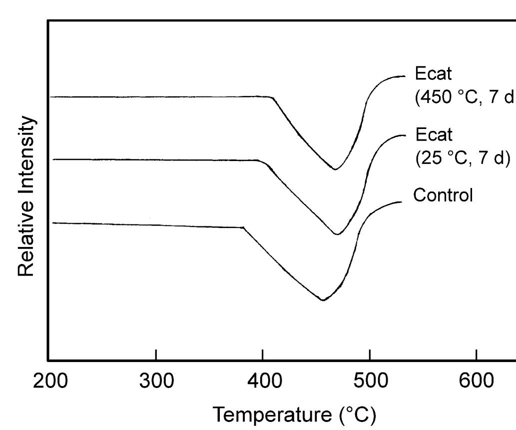

Fig. 3. DSC curves of the pastes [water/(0.9 CH + 0.1 additive) = 0.8] cured at 7 days.

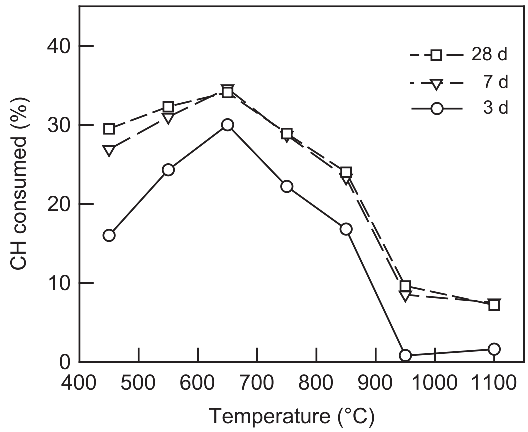

Fig. 4. Percentage of CH in hydrated pastes containing calcined Ecat.

calcination temperature on the percentage of CH consumed in hydrated pastes containing treated Ecat for 3–28 days. The amount of CH in the control was defined as 100%. As temperature increases, the amount of CH consumed increases initially, reaches the maximum value, and then decreases afterwards. Apparently, Ecat calcined at about 650 °C exhibits the highest pozzolanic activity.

Separately, the AI of the raw or treated Ecat was determined. The procedure to determine AI was described in Section 2.4. The mixture proportions of mixes containing different additives, the compressive strength of specimens, and the calculated AI value of each additive are listed in Table 2. It is clear that the mortar with treated Ecat (calcined at 650 °C for 1 h) shows higher AI value than that with untreated catalyst.

Fig. 5 shows the effect of calcination temperature on the compressive strength of mortars incorporated with 10% treated Ecat. Similar trend with that in Fig. 4 was observed. That is, the compressive strength is increased with temperature first, reaches a maximum value at about 650 °C, and then decreases subsequently.

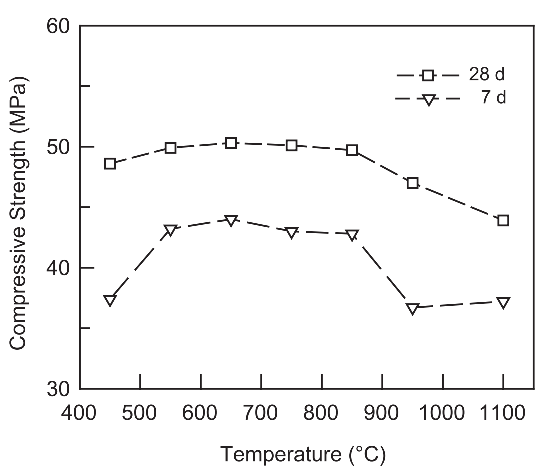

Fig. 5. Effect of calcination temperature on the compressive strength of mortars with 10% treated Ecat.

The reasons that Ecat calcined at high temperatures shows improved activity and higher compressive strength of the resulting mortars could be twofold: one is the change of mineralogy and the other is the change of particle characteristics.

Fig. 6 shows the XRD diagram of Ecat particles calcined at various temperatures for 1 h. As mentioned before, the uncalcined Ecat possesses mainly Faujasite phase (see Fig. 2). When the catalyst was thermally treated, the intensity of the phases appears to be changed gradually with increasing temperature. For temperatures below 850 °C, the calcined catalyst possesses similar crystalline phases as the untreated, but with lower intensity. When the temperature is up to 950 °C or above, the crystalline phases of Ecat change and become mainly mullite phase. Although the crystalline phases remain almost the same from 450 to 850 °C, the crystal lattice structure of Ecat would be like that of metakaolin to be broken down, or partly broken down, due to dehydration and forms a transition phase. This leads to an improved activity of the treated catalyst [22].

Meanwhile, the particle size and specific surface area of treated Ecat were measured, as is shown in Fig. 7. The particle size of the calcined catalyst in the temperature range of 25–1000 °C was found almost the same as that of the untreated. Similarly, the specific surface area of the calcined catalyst is also close to that of the untreated up to 850 °C. However, the specific surface area of the treated Ecat was found to decrease sharply afterwards. This is attributed to the sintering of particles and closing of the pore channels. As a result, the activity of the catalyst declines greatly from 850 °C, and the compressive strength of mortars with Ecat calcined at 950–1100° is clearly less than those at lower temperatures, i.e., 550–850 °C (see Figs. 4 and 5).

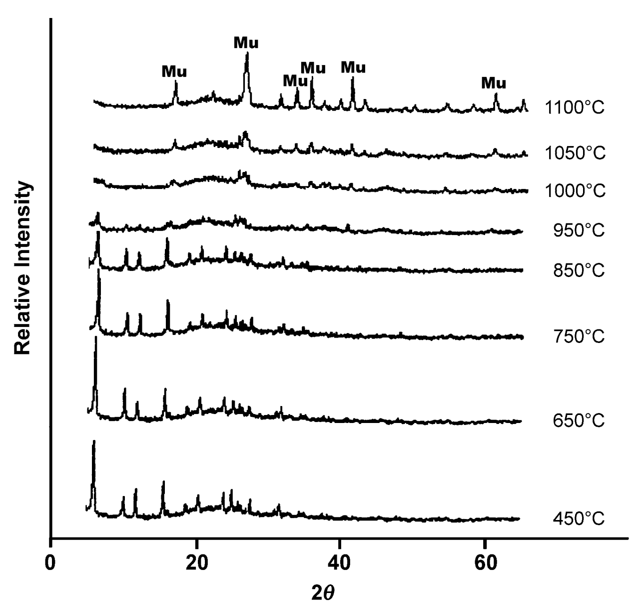

Fig. 6. XRD diagram of calcined Ecat.

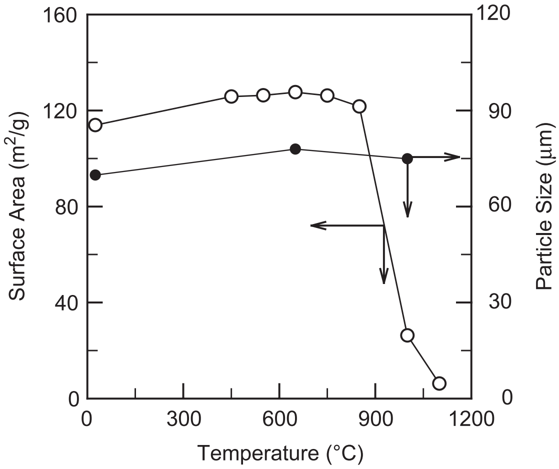

Fig. 7. Particle size and specific surface area of treated Ecat.

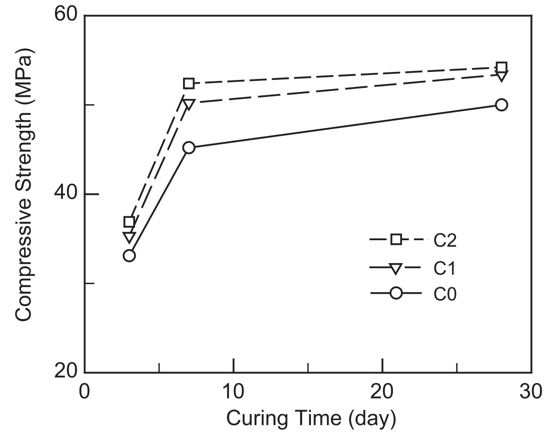

Fig. 9. Effect of treated Ecat on the compressive strength of concrete.

Fig. 8 shows the effect of treated Ecat on the compressive strength of mortars (W/B = 0.42) cured at 3, 7, and 28 days, respectively. As expected, the compressive strength of mortars with or without treated catalyst was found to increase with curing time. The compressive strengths of mortars containing 10% Ecat without any treatment (named as M0) are 26, 34.3, and 40.4 MPa, cured at 3, 7, and 28 days, respectively. These values are lower than those of the control, i.e., mortars without the incorporation of waste catalyst. Mortars with 10% catalyst calcined at 650 °C for 1 h (named as M1) show higher strength values than those with the untreated. The compressive strengths of M1 are 28, 40.4, and 47.1 MPa, cured at 3, 7, and 28 days, respectively. These values are 8%, 18%, and 17%, respectively, greater than those of M0. They are −13%, 12%, and 7% greater than those of the control. The improvement of the material strength is due to the enhancement of the pozzolanic activity of the catalyst after calcination. The compressive strengths of mortars could be further improved if the mix contains calcined catalyst that was further ground. The AI value of the catalyst after calcination at 650 °C for 1 h and ball milled for 2 h is 90.8, which is higher than that of the calcined one without any grinding (see Table 2). M2 in Fig. 8 is the mortar incorporated with 10% calcined and ground Ecat. After a 2-h grinding, the average particle size of the calcined catalyst is reduced from 67.4 to 3.2 μm. The compressive strengths of M2 are 31.9, 43.1, and 49.7 MPa, cured at 3, 7, and 28 days, respectively. These values are 23%, 26%, and 23%, respectively, than those of M0. Obviously, further improvement in pozzolanic activity and the resulting strength was achieved because of the increased fineness of the catalyst.

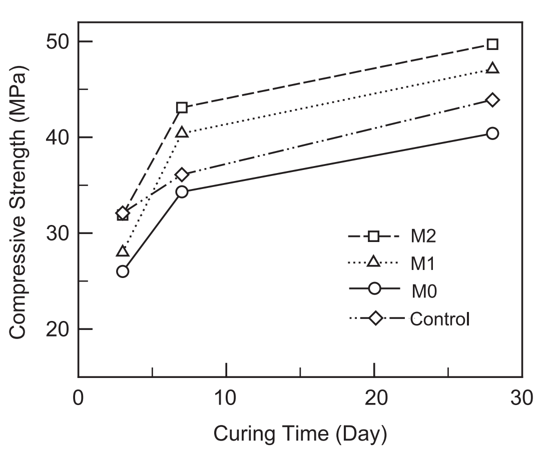

Fig. 8. Effect of treated Ecat on the compressive strength of mortars.

Similarly, concrete with 10% Ecat after calcination and/or ball milling also exhibits higher strength value than that with 10% untreated catalyst, as is shown in Fig. 9. The mix design of tested concrete is listed in Table 3. The compressive strengths of concrete containing untreated Ecat (named as C0) are 33.1, 45.2, and 50 MPa, cured at 3, 7, and 28 days, respectively. Concrete with 10% catalyst calcined at 650 °C for 1 h (named as C1) shows higher strength value than those with 10% untreated. The compressive strengths of C1 are 35.3, 50.2, and 53.4 MPa, cured at 3, 7, and 28 days, respectively. These values are 7%, 11%, and 7%, respectively, greater than those of C0. Concrete with 10% catalyst calcined at 650 °C for 1 h and ground for 2 h (named as C2) shows even higher strength values. The compressive strengths of C2 are 36.9, 52.4, and 54.2 MPa, cured at 3, 7, and 28 days, respectively. These values are 11%, 16%, and 8%, respectively, greater than those of C0.

4. Conclusions

Ecat is one spent FCC catalyst from oil companies and shows pozzolanic activity. This waste material has been considered as a concrete additive. This study indicates that its pozzolanic activity could be improved by heat treatment at 450–850 °C and/or grinding. Therefore, the treated waste catalyst could improve the compressive strength of the resulting cementitious materials. Mortars with 10% calcined

(M1) and calcined/ground Ecat (M2) at 3–28 days exhibit strength 8–18% and 23–26% greater than those with the untreated (M0). Concrete with a 10% calcined (C1) and calcined/ground Ecat (C2) at 3–28 days exhibit strength 7–11% and 8–16% greater than those with the untreated (C0).

Acknowledgements

The authors are grateful for the support of this work by the National Science Council of The Republic of China (Contract # NSC-91-2211-E-003-001).

References

[1] P.C. Aitcin, High-Performance Concrete, E&FN SPON, New York, 1998.
[2] M.I. Sanchez 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.
[3] C.L. Hwang, D.H. Sheen, The effect of blast-furnace slag and fly ash on the hydration of Portland cement, Cem. Concr. Res. 21 (4) (1991) 410–425.
[4] 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.
[5] B. Pacewska, M. Bukowska, I. Wilinska, M. Swat, Modification of the properties of concrete by a new pozzolan—a waste catalyst from the catalytic process in a fluidized bed, Cem. Concr. Res. 32 (1) (2002) 145–152.
[6] B. Pacewska, I. Wilinska, M. Bukowska, W. Nocun-Wczelik, Effect of waste aluminosilicate material on cement hydration and properties of cement mortars, Cem. Concr. Res. 32 (11) (2002) 1823–1830.
[7] B. Pacewska, I. Wilinska, M. Bukowska, Hydration of cement slurry in the presence of spent cracking catalyst, J. Therm. Anal. Calorim. 60 (2000) 71–78.
[8] B. Pacewska, I. Wilinska, J. Kubissa, Use of spent catalyst from catalytic cracking in fluidized bed as a new concrete additive, Thermochim. Acta 322 (2) (1998) 175–181.
[9] J. Paya, J. Monzo, M.V. Borrachero, S. Velazquez, Evaluation of the pozzolanic activity of fluid catalytic cracking catalyst residue (FC3R). Thermogravimetric analysis studies on FC3R-Portland cement pastes, Cem. Concr. Res. 33 (4) (2003) 603–609.
[10] J. Paya, J. Monzo, M.V. Borrachero, Fluid catalytic cracking residue (FC3R): An excellent mineral by-product for improving early-strength development of cement mixtures, Cem. Concr. Res. 29 (11) (1999) 1773–1779.
[11] N. Su, H.Y. Fang, Z.H. Chen, F.S. Liu, Reuse of waste catalysts from petrochemical industries for cement substitution, Cem. Concr. Res. 30 (11) (2000) 1773–1783.
[12] N. Su, Z.H. Chen, H.Y. Fang, Reuse of spent catalysts as fine aggregate in cement mortar, Cem. Concr. Compos. 23 (1) (2001) 111–118.
[13] J. Paya, J. Monzo, M.V. Borrachero, Physical, chemical and mechanical properties of fluid catalytic cracking residue (FC3R) cements, Cem. Concr. Res. 31 (1) (2001) 57–61.
[14] J.H. Wu, W.L. Wu, K.C. Hsu, The effect of waste oil-cracking catalyst on the compressive strength of cement pastes and mortars, Cem. Concr. Res. 33 (2) (2003) 245–253.
[15] S.Y.N. Chan, X. Ji, Comparative study of the initial surface absorption and chloride diffusion of high performance zeolite, silica fume and PFA concretes, Cem. Concr. Compos. 21 (4) (1999) 293–300.
[16] K.C. Hsu, Y.S. Tseng, F.F. Ku, N. Su, Oil cracking catalyst as an active pozzolanic material for superplasticized mortars, Cem. Concr. Res. 31 (12) (2001) 1815–1820.
[17] H.L. Chen, Y.S. Tseng, K.C. Hsu, Spent FCC catalyst as a pozzolanic material for high-performance mortars, Appl. Clay Sci. 23 (2004) (in press).
[18] C. He, E. Makovicky, B. Osbæck, Thermal treatment and pozzolanic activity of sepiolit, Cem. Concr. Compos. 10 (5) (1996) 337–349.
[19] M.S. Morsy, A.F. Galal, S.A. Abo-El-Enein, Effect of temperature on phase composition and microstructure of artificial pozzolana–cement pastes containing burnt kaolinite clay, Cem. Concr. Res. 28 (8) (1998) 1157–1163.
[20] G. Kakali, T. Perraki, S. Tsivilis, E. Badoginannis, Thermal treatment of kaolin: The effect of mineralogy on the pozzolanic activity, Cem. Concr. Compos. 20 (1) (2001) 73–80.
[21] W. Sha, G.B. Pereira, Differential scanning calorimetry study of ordinary Portland cement paste containing metakaolin and theoretical approach of metakaolin activity, Cem. Concr. Compos. 23 (6) (2001) 455–461.
[22] B.B. Sabir, S. Wild, J. Bai, Metakaolin and calcined clays as pozzolans for concrete: A review, Cem. Concr. Compos. 23 (6) (2001) 441–454.
[23] W. Sha, E.A. O'Neill, Z. Guo, Differential scanning calorimetry study of ordinary Portland cement, Cem. Concr. Res. 29 (9) (1999) 1487–1489.