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Reuse of spent catalyst as fine aggregate in cement mortar

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Abstract

This study examined the feasibility of reusing spent zeolite catalyst, after fluidized catalytic cracking, as a substitute for fine aggregate (sand) in cement mortars. The tested result shows that spent catalyst can replace up to 10% of fine aggregate without decreasing the mortar strength. In fact, the substituted mortars show higher compressive strength than the unsubstituted samples. The flowability of the fresh mortars decreases with increasing substitution level and the mortars incorporated with spent catalyst show less bleeding. In the hardened state, the water absorption of the resulting mortar increases with longer curing age, higher substitution level and smaller water-to-cement (W/C) ratio. Toxicity characteristic leaching procedure (TCLP) analysis confirms that the spent catalyst meets the standard, and thus should be classified as general non-hazardous industrial waste.

Keywords: Spent catalyst; Reuse; Compressive strength; Workability; Mortar; Fine aggregate

1. Introduction

Taiwan is a small but densely populated island, therefore the best 'strategy for solid waste management is to work towards the 5 Rs of reduction, recovery, recycle, reuse, and research. Zeolite catalyst is an essential catalyst. Its use makes up 1/5 of the world catalyst market [1]. This catalyst has been widely used in oil refinery and petrochemical industries and there is a significant quantity of spent catalysts produced. After reaction in the fluidized catalytic cracking unit (FCCU) spent catalysts are removed from the bed and replaced by new ones in order to maintain the catalytic activity. These spent catalysts are called equilibrium catalysts (Ecat). The Ecat from residual oil cracking units (ROCU) alone amounts to 6–9 metric tons/day [2]. Furimsky pointed out that on a world scale about 400,000 metric tons of spent catalysts from FCCU are produced annually [3]. As for the possible alternatives of reusing these spent catalysts, Hsu [4] reported that spent catalysts from ROCU can withstand temperatures of more than 1750°C. Therefore, it can be used for manufacturing fireproof materials, or it can be added to clay and heat-treated to form valuable building materials such as ceramic tiles, refractory bricks and insulation bricks. The adsorption capacity for volatile organic compounds (VOCs) of products manufactured from recycled residual oil cracking (ROC) and fluidized catalytic cracking (FCC) spent catalysts was reported to be 1/3 that of activated charcoal [5]. Lin [6] reported that the stiffness of asphalt concrete could be greatly improved by combining waste fly ash, particulate collected by a bagged dust collector in a dry mix process at an asphalt mix plant, and spent catalysts in different proportions. Furimsky [3] concluded that the best way to recycle spent catalysts is to utilize them in concrete. These wastes are in fact of great value to the concrete industries. For Portland cement, which is produced from the reaction of limestone and clay in a high-temperature kiln, spent catalysts can make up 6% of the cementitious raw materials with the rest being 75% limestone and 19% clay. Hsu [4] indicated that 80% of ROC spent catalysts were SiO_2 and Al_2O_3, while Furimsky reported that FCC Ecat contained about 60-wt% of SiO_2 and 40-wt% of Al_2O_3 together with some other impurities in minute quantities [3].

Tests performed on these spent catalysts revealed that they are not hazardous. It was reported that spent catalysts were also used in manufacturing bricks. These

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bricks containing 5% of spent catalysts were shown to be environmentally safe. Ceramic products made from materials using FCC spent catalysts were compared with those made from kaolin plus other materials and they were found to be of the same quality [3]. Su [7] reported that mortars with 5–10% ROC Ecat substituting for cement show higher compressive strengths than the unsubstituted control group. Ujike [8] pointed out that compressive strength of concrete with water binder ratio of 50% and 65% is hardly affected by the incorporation of artificial zeolite converted from fly ash. The air permeability and chloride penetration are lowered by the use of zeolite.

Most research involving the recycling of Ecat [9–14] deals with the extraction of useful metals for making new catalysts. After repeated use, they are finally solidified with cement and buried in landfill. Recycled material is also taken as raw materials for manufacturing cement, ceramics, bricks or tiles. Recently in Taiwan, most spent catalysts are stored in the oil refining company, as less land is available to bury them. Nowadays, the fine aggregate is seriously lacking in Taiwan. In fact, the great demand for sand as a component of building materials has led to over mining, thus causing problems such as the exposure of bridge foundations. Although the ROC Ecat can be partially substituted for cement in mortars and concrete to achieve higher economic value, it would be very worthwhile in using the catalyst to replace part of the fine aggregate since the cement dosage is far less than the fine aggregate dosage in concrete mixture proportioning. In this study, these spent catalysts were added to the mortars to substitute part of the fine aggregate. The chemical and physical properties of the ROC Ecat were analyzed and the engineering properties of these substitute mortars were investigated to study the feasibility of using the resulting mortars as a construction material.

2. Materials and experimental program

2.1. Materials

Type I Portland cement from Taiwan Cement Company was used in this study. Its physical and chemical properties (Table 1) meet the requirements of ASTM C150 [15]. Standard sand from Ottawa and further processed in the US, with physical properties and size gradation (Table 2) meeting the requirements of ASTM C778 [15] was used. The spent catalysts came from the plant of the China Petroleum Company in Kaohsiung, Taiwan. Their absorption capacity (from the oven-dry to the SSD condition) is 31%; other properties are presented in Section 3 of this paper.

Table 1
Chemical composition and physical properties of cement

Test item		Test result	ASTM C150
Chemical composition			
SiO_2 (%)		21.22	–
Al_2O_3 (%)		5.13	–
Fe_2O_3 (%)		2.91	–
CaO (%)		62.48	–
MgO (%)		3.80	$\leqslant$6.0
SO_3 (%)		2.14	$\leqslant$3.5
Free-lime (%)		0.94	–
Loss on ignition (%)		0.91	$\leqslant$3.0
Insoluble residue (%)		0.22	$\leqslant$4.30
C_3A (%)		44.2	–
C_2A (%)		27.3	–
C_3A (%)		8.7	–
C_4AF (%)		8.9	–
Physical properties			
Sp.gr.		3.15	–
Fineness (air permeability test) (m^2/kg)		346	$\geqslant$280
After #325 sieving (%)		4.9	–
Time of setting (Vicat test)	Initial set (min)	169	$\geqslant$45; $\leqslant$375
	Final set (min)	270	–
Autoclave expansion (%)		0.20	$\leqslant$0.8
Compressive strength	3 days (MPa)	20.5	$\geqslant$12.0
	7 days (MPa)	31.9	$\geqslant$19.0
Air content of mortar (%)		6.1	$\leqslant$12.0

Table 2
Physical properties and size gradation of standard sand

Properties	Size gradation	
	Sieve	Pass (%)
Sp.gr.	No. 16	100
Absorptivity (%)	No. 30	99.7
Fine modulus	No. 50	20
	No. 100	17

2.2. Experiment procedures

Mortar specimens of $5 \times 5 \times 5$ cm^3 were prepared by mixing cement and fine aggregates (Ottawa sand and ROC Ecat), then these specimens were cured in saturated lime water at 23°C for 7, 14, 28 and 56 days according to ASTM C109 [15]. The levels of sand substitution used were 5%, 10% and 15%, with 0% substitution acting as the control group. The W/C ratios of mortars were 0.42, 0.485, and 0.55 and the cement-

Table 3
Mixture proportioning of mortar samples

Materials(g)	Fine aggregate substitution by ROC Ecat				
	0%	5%	10%	15%	W/C
Cement	723	723	723	723	0.42
Mixed water	304	304	304	304	
Standard sand	1989	1890	1790	1691	
ROC Ecat	0	99	199	298	
Cement	712	712	712	712	0.485
Mixed water	345	345	345	345	
Standard sand	1959	1861	1763	1665	
ROC Ecat	0	98	196	294	
Cement	701	701	701	701	0.55
Mixed water	386	386	386	386	
Standard sand	1929	1833	1736	1640	
ROC Ecat	0	96	193	289	

to-sand ratio was 1:2.75 (by weight). The mixture proportion is shown in Table 3.

2.2.1. Analysis of ROC Ecat properties

The composition and microstructure of ROC Ecat were analyzed by using standard chemical analysis method and scanning electron microscopy (SEM) (JSM-5410LV, Jeol, Japan). A Particle size analyzer (Malvern Instruments, England) determined the particle size distribution. The specific surface area was measured by a mercury porosimeter (Model ASAP 2010, Micromeritics Instrument, USA). Crystalline phases identified using X-ray powder diffraction (Siemens D5000 diffractiometer, Germany) with a scanning rate of 1°/min.

2.2.2. Tests on fresh mortar

Both the flow table test and bleeding test were carried out on the mortar. The flow table test procedure was according to ASTM C230 [15], and the bleeding capacity of mortar was measured according to ASTM C243 [15].

2.2.3. Tests on hardened mortar

Both the compressive strength and water absorption of the mortars were determined. An ELE 200-ton compressive test machine was used to test mortar samples, which had been cured in saturated lime solution at 23 ± 1°C for 7, 14, 28, and 56 days according ASTM C31 [15].

The method used to determine the water absorption was according to ASTM C642 [15] or the ISRM suggested methods [16]. The mass "A" was measured after drying at 110 ± 5°C for sufficient time to remove all uncombined water. Then, the mortar samples were immersed in lime water at 23 ± 1.7°C for 7, 14, 28 and 56 days. The samples were removed and surface-dried using a moist cloth. Care was taken to remove only surface water and to ensure that no mortar fragments were lost. The mass of the surface-dried sample was "B" [16].

$$\text{Water absorption }(\%) = \frac{B - A}{A} \times 100\%.$$

2.2.4. Toxicity test

The toxic content test was conducted in accordance with the toxicity characteristic leaching procedure (TCLP) specified by the Environment Protection Agency (EPA) of Taiwan [17]. The test is briefly described as follows:

Prepare two extraction solvents: For example, place 5.7 ml HCOOH and 64.3 ml 1.0 N NaOH in a 1000 ml container and dilute to a pH value of 4.93 ± 0.5 to prepare the first solvent. The second solvent is obtained in a similar manner.

Choose the proper extraction solvent: Place a 5 g sample into a 500 ml container, then add 96.5 ml deionized water and measure the pH value after thorough mixing. From the pH value, decide which extraction solvent to use.

Extract the metallic content:

1. Place 100 g sample into a 2 l extraction bottle and add 2 l extraction solvent (solid/liquid ratio = 1:20).
2. Place the fore-prepared solution into a spinning extractor and spin for 18 ± 2 h at 30 rpm.
3. Filter the solution with a 0.45 μm membrane and acidify to pH < 2 with HNO_3. Analyze the heavy metal content by inductively coupled plasma atomic emission spectroscopy (ICP–AES).

3. Results and discussion

3.1. Basic properties of spent catalysts

Table 4 shows both chemical composition and physical properties of ROC Ecat. It is revealed from this table that the spent catalysts are mainly made up of SiO_2 and Al_2O_3. As can be seen, these two components account for over 90% of the total weight in Ecat. These results are in good agreement with other reports [3,4,18].

Fig. 1 and Table 4 show the results of element analysis of ROC Ecat. The main elements were found to be Si, Al, and O with small amounts of Fe, Mg, Ti, V, Ni and S.

Fig. 2 shows the particle size distribution of ROC Ecat which ranges from 10 to 130 μm with an average diameter of 68.5 μm. Hsu [4] pointed out that 85% of the ROC Ecat was less than 100 μm. Our result seems to be in agreement with their finding.

Fig. 3 illustrates the ignition loss of ROC Ecat at 500°C, 600°C and 700°C. The maximum ignition loss is

Table 4
The characteristic of ROC Ecat

Test item	Test result
Component	
Ignition loss (%)	3.31
SiO_2 (%)	51.69
Al_2O_3 (%)	41.12
Fe_2O_3 (%)	1.08
CaO (%)	1.73
MgO (%)	0.41
SO_3 (%)	0.48
Na_2O (%)	0.42
K_2O (%)	0.06
Element analysis	
Al (%)	21.95
Si (%)	24.73
Fe (%)	1.16
Mg (%)	0.73
Ti (%)	0.63
V (%)	0.47
Ni (%)	0.42
S (%)	0.20
O (%)	49.71
Physical properties	
Bulk density (g/cm^3)	0.88
Sp.gr.	2.48
Specific surface area (m^2/g)	249
Pore volume (cm^3/g)	0.265

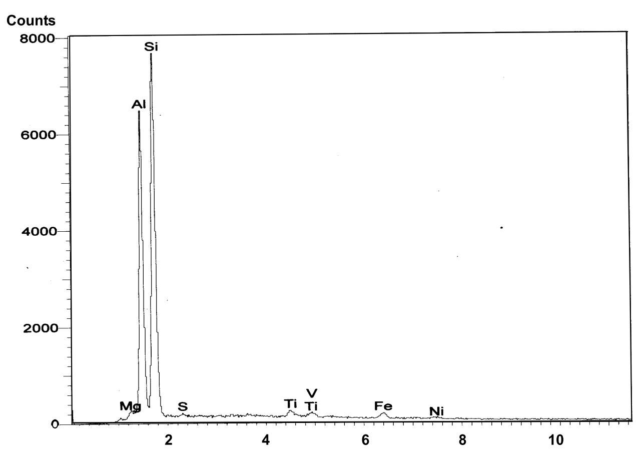

Fig. 1. Analysis of ROC Ecat with EDS.

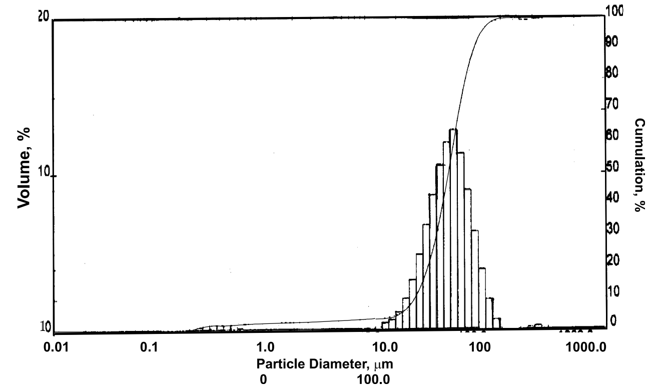

Fig. 2. Size distribution on ROC spent catalysts.

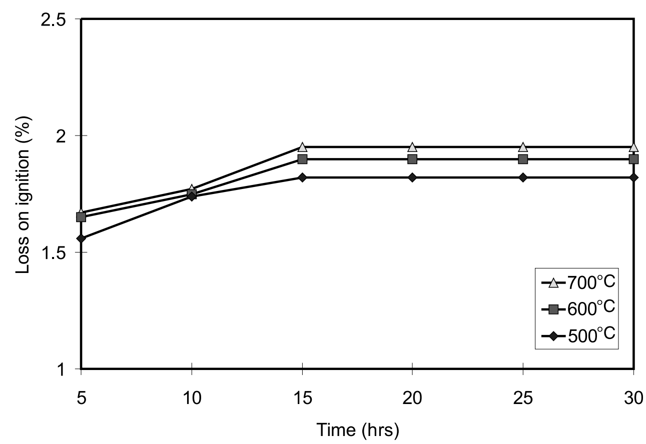

Fig. 3. Loss on ignition of ROC Ecat.

1.93% at 700°C, indicating that the contents of organic materials and impurities are low. The presence of organic materials usually interferes with cement hydration, retards hardening and affects strength development of concrete. Their small quantity implies that such effects would be insignificant.

Ecat has a bulk density of 0.88 g/cm^3 and a specific gravity of 2.48, which are lower than those of standard sand. It should be noted, that although the particle size of Ecat is relatively large, the specific surface of the Ecat is very large (249 m^2/g), and is much larger than that of standard sand. This is because the catalyst is very porous, as seen from the SEM micrograph of ROC Ecat (in Fig. 4). Also, ROC Ecat appears to be granular. Liu [19] reported that ROC Ecat is made up of many tiny particles sintered or agglomerated together. This leads to a highly porous surface structure (observed under the microscope), thus making the catalyst ideal for catalytic cracking reaction.

Fig. 5 illustrates the X-ray diffraction plot of ROC Ecat. According to the database of Joint Committee on Powder Diffraction Standards, 1989 (JCPDS), the ROC Ecat crystal structure is close to that of Faujasite (Sodium Aluminate Silicate Hydrate, $Na_2O \cdot Al_2O_3 \cdot 4.7SiO_2 \cdot xH_2O$) [20].

Finally, a TCLP analysis was carried out. The results are shown in Table 5. The amounts of heavy metals leached from the spent catalyst were found to be in low concentration (Cd: not detected, Cr: 0.0692 mg/l, Pb: 0.1261 mg/l) and met the regulatory standard in Taiwan (Cd < 1 mg/l, Cr < 5 mg/l, Pb < 5 mg/l). Therefore, the catalysts are considered as non-hazardous and can be classified as general industrial wastes.

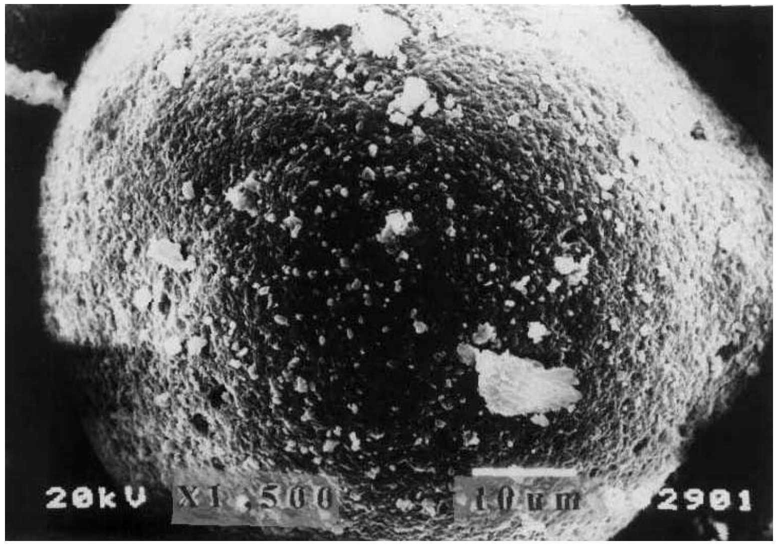

Fig. 4. Microstructure of ROC Ecat.

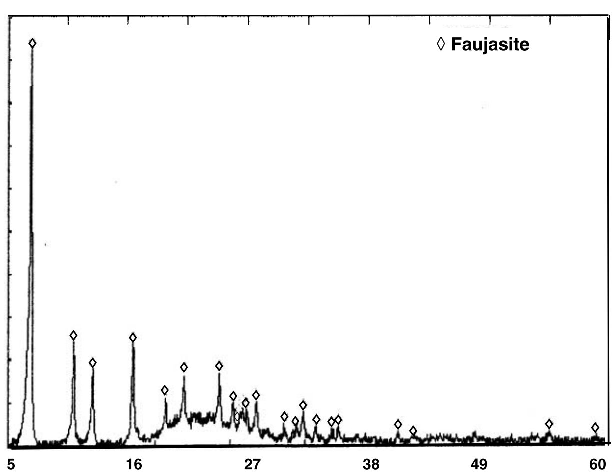

Fig. 5. X-ray diffraction plot of ROC Ecot.

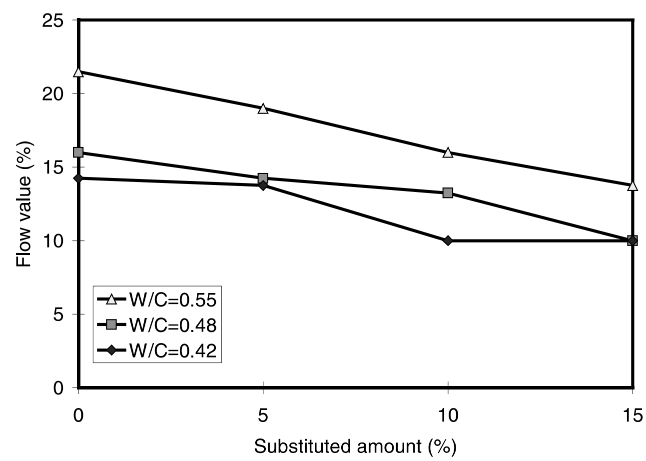

Fig. 6. Changes in flow value of mortars with sand substituted by ROC Ecat.

Table 5
TCLP analysis of ROC spent catalyst (unit: mg/l)

	Cd	Cr	Pb	Ni
ROC Ecat	ND[a]	0.0692	0.1261	0.7424
Regulatory standard	1.0	5.0	5.0	–

[a] ND: Not detected.

3.2. Characteristics of fresh mortars

Fig. 6 shows the flow value (ASTM C230) of mortars with part of the sand substituted by ROC Ecat. As expected the flow value increased with higher W/C ratio, but decreased with increased substitution of sand with ROC Ecat, the latter being due to the high porosity of the spent catalyst. When $W/C = 0.42$, there is no flow for mortars with a substitution $\geqslant 10\%$. Thus to maintain good workability, no more than 5% of sand substitution is recommended at such a low W/C ratio.

Fig. 7 shows the bleeding capacity of mortars. Generally, bleeding capacity increased with higher W/C ratio, but decreased with greater substitution levels. For mortars with $W/C = 0.55$, bleeding capacity decreased from 14.43% to 0% as substitution increased from 0% to 15%. For mortars with $W/C = 0.485$, bleeding capacity decreased from 7.46% to 0%. For mortars with $W/C = 0.42$, no bleeding occurred at any of the substitution levels. As mentioned earlier, the particle size of ROC Ecat is much smaller than that of sand and the specific surface area of Ecat is much higher than that of

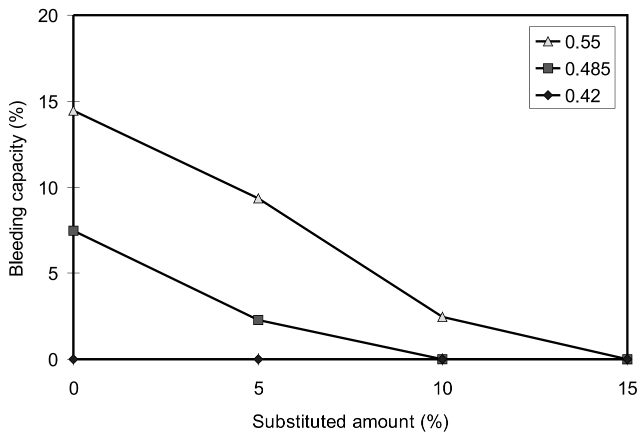

Fig. 7. Bleeding capacity of mortars with sand substituted by ROC Ecat.

sand. Therefore, substitution of Ecat in mortars would be helpful in reducing the bleeding. Concrete with reduced bleeding is generally durable [21].

3.3. Characteristics of hardened mortars

The mortars with 5% and 10% substitution ($W/C = 0.55$) showed compressive strengths 18% and 34% higher than that of the control after 7 days of curing (Fig. 8), 13–19% and 19–31% higher than that of the control at 28 days and 56 days of curing, respectively. This indicates that the ROC Ecat has induced Pozzolanic reaction in the mortars. The mortars with 15% substitution showed much lower strength throughout the test period. This is because at this high level of substitution the spent catalyst absorbs a lot of water, which leads to poor workability and compaction.

The mortars with 5% substitution ($W/C = 0.485$) have compressive strengths 13%, 12% and 19% higher than those of the control after 7 days, 28 days and 56 days of curing, respectively. The mortars with 10% substitution show similar strengths to the control after 7 days of curing. However, after 28 days and 56 days of curing, strengths are 47% and 25% higher than that of the control, which is attributed to the Pozzolanic reaction of ROC Ecat. The mortars with 5% and 10% substitution showed a significant increase in strength after 28 days of curing. The mortars with 15% substitution showed poor compressive strength due to the lack of water. The consistency of these mortars was poor during mixing.

For mortars with $W/C = 0.42$, the mortars with 5% substitution show -8% and $+7\%$ strength relative to the control at, respectively, 7 days and 56 days of curing. The mortars with 10% and 15% substitution showed strength 28% and 64% lower than the control, respectively, after 28 days of curing. This is because at low

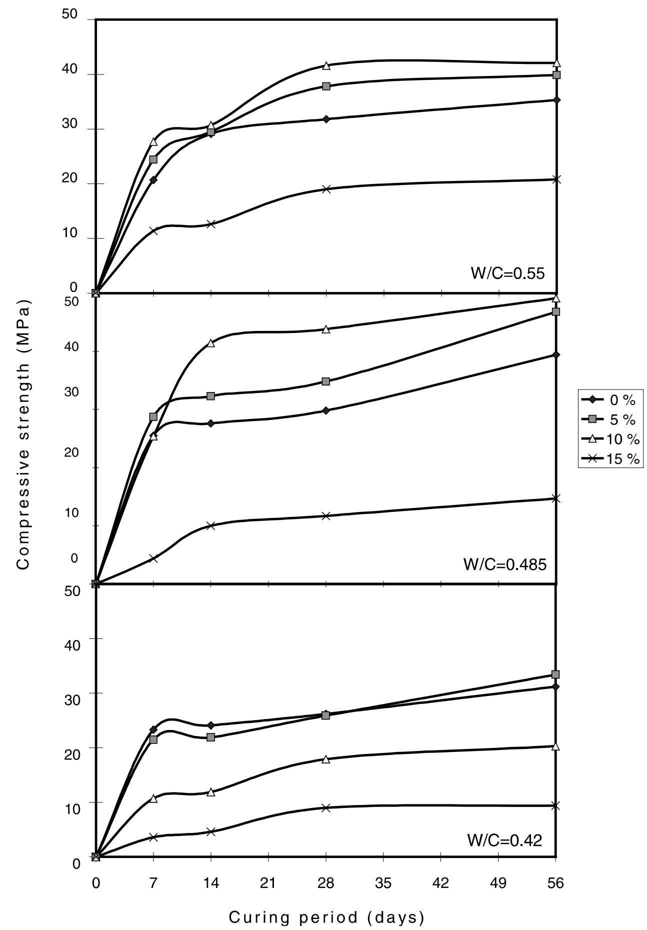

Fig. 8. Changes in compressive strength of motars with sand substituted by ROC Ecat.

W/C ratios, the quantity of available water in mortar samples is much reduced due to water absorption by the ROC Ecat, leading to low workability and poor compaction.

Water absorption is correlated with porosity, and also with other properties such as degree of weathering or alteration. Fig. 9 illustrates changes in the water absorption of mortars with sand substituted by Ecat at different W/C ratios. The water absorption increases with increasing curing time and increases with decreasing W/C ratio. When $W/C = 0.55$ and with 15% substitution, the absorption is 9.4% in 7 days. For mortars with 5% and 10% substitution, it is close to that of the control. When $W/C = 0.485$, the absorption of mortars with 15% substitution is 13.2% in 7 days. When $W/C = 0.42$, the absorption increases significantly with increased substitution level and longer curing periods. After 56 days of curing, mortars ($W/C = 0.42$) with 0%, 5%, 10%, and 15% substitution showed 4.6%, 6.9%, 11.9%, and 16.1% absorption, respectively. At all W/C ratios, mortars with 15% substitution showed the highest absorption indicating that these mortars tend to dry

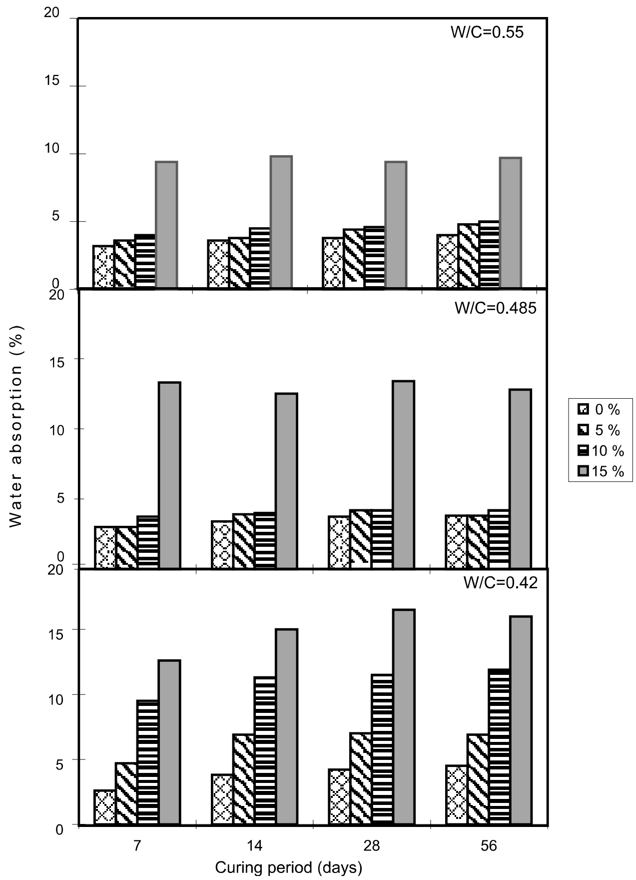

Fig. 9. Changes in water absorption of mortars with sand substituted by ROC Ecat.

up. Again, this is because Ecat is porous, resulting in high water absorption.

3.4. TCLP analysis

Results of the TCLP analysis are shown in Table 6. As can be seen, the concentrations of toxic materials leached from mortars with 5–15% substitution were all lower than the standard specified by the EPA of Taiwan for hazardous substances. Compared with the results in Table 5, the leached concentration of toxic materials is lower than that of ROC Ecat. It is clear that it is due to the additional effect provided by cement mortars.

Table 6
TCLP analysis on ROC Ecat-substituted mortars (unit: mg/l)

Substitution	Cd	Cr	Pb	Ni	W/C
5%	ND	0.116	ND	ND	0.42
10%	ND	0.139	ND	ND	
15%	ND	0.185	ND	ND	
5%	ND	0.116	0.014	ND	0.485
10%	ND	0.139	0.053	0.037	
15%	ND	0.185	0.007	ND	
5%	ND	0.301	0.060	ND	0.55
10%	ND	0.162	0.028	0.076	
15%	0.003	0.162	0.053	0.068	
Regulatory standard	1.0	5.0	5.0	–	

4. Conclusions

Based on the analysis of the test data presented, the following conclusions are drawn:

1. The analyses indicate that the spent catalyst is mainly composed of SiO_2 and Al_2O_3. The particle size distribution is in the range 10–130 μm. Spent catalyst is porous and has very large specific surface (249 m^2/g). The absorption capacity of ROC Ecat is 31%. Furthermore, a TCLP analysis shows that the spent catalyst could be classified in general as non-hazardous industrial waste.
2. The flowability and bleeding of mortar increase with W/C ratio but decrease with the percent of sand substituted by ROC Ecat.
3. In general, when $W/C = 0.55$ or 0.485, the mortars with 5% or 10% substitution show higher compressive strength than the control. This is attributed to the Pozzolanic activity of the spent catalyst. With 15% substitution, the compressive strength is much lower than that of the control due to poor compaction of the substituted mortars.

5. Suggestion for further research

Although this study showed that the spent catalyst could be used as a substitute for sand, the ROC Ecat has also been considered as an additional source for ultrafine material to partially replace cement [7,8]. Other ways of valorization could be further investigated, for example, replacement of silica fume in high strength concrete. Due to the porous structure, hence high water absorption of ROC Ecat, it is recommended that prewetting of ROC Ecat is done before casting mortars or concrete. The shrinkage of mortars with ROC Ecat deserves further study.

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