



Reuse of waste catalysts from petrochemical industries for cement substitution

Nan Su*, Hung-Yuan Fang, Zong-Huei Chen, Fu-Shung Liu

National Yunlin University of Science and Technology, 123, Sec. 3, University Road, Touliu, Yunlin 640, Taiwan, ROC

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Abstract

Zeolite catalysts have been widely used in oil refinery and petrochemical industries. Two types of waste catalysts, equilibrium catalyst (Ecat), and electrostatic precipitator catalyst (EPcat), can be obtained after fluid catalytic cracking. This study analyzes the properties of these waste catalysts and examines the feasibility of reusing them to substitute part of the cement required in mortar preparation. These waste catalysts are found to comprise mainly SiO_2 and Al_2O_3 . Their catalytic structure is coarse and porous, while their crystal pattern is similar to that of Faujasite zeolite. Their specific surface area varies with different types of catalysts. Their specific gravity is 2.48 and their apparent bulk density is about 0.88 g/cm^3 . They can substitute up to 15% of the cement content in mortar without sacrificing the quality of concrete. In fact, the substituted concrete shows a greater compressive strength, 15% higher than that without substitution. The setting time of the fresh mortar becomes shorter with increasing amount of cement substituted; while the spread flow value decreases with increasing percentage of cement substitution. Bleeding is reduced and the hydration heat of mortars with 10% and 15% substitution are close to that without substitution because these waste catalysts are exothermic. The water absorptivity in hardened mortar increases with longer curing age, greater substitution percentage, and smaller water to cement ratio (W/C). X-ray diffraction analysis reveals that when $\text{W/C} = 0.485$ and curing age = 28 days, the crystal patterns of mortars prepared with different amount of cement substituted by Ecat are similar. According to the results of TCLP analysis, these spent catalysts should be classified as general non-hazardous industrial waste and they meet the effluent standard. Therefore, reuse of these industrial waste catalysts is feasible and will not result in pollution due to the leaching of heavy metals. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Waste catalyst; Reuse; Mortar

1. Introduction

Taiwan is a small but densely populated island, the 5R's — reduction, recovery, recycle, reuse, and research play important roles in waste management. Zeolite catalysts are essential catalyst types. Its use makes up one-fifth of the world catalyst market [1]. Zeolite catalysts have been widely used in oil refinery and petrochemical industries and there is a significant quantity of waste catalysts produced. Two types of waste catalysts can be obtained after catalytic reaction in the fluid catalytic cracking unit (FCCU). One is called equilibrium catalyst (Ecat). These waste catalysts are to be replaced by new ones in order to maintain the catalytic activity. The

other type is called electrostatic precipitator catalyst (EPcat). These waste catalysts come from the cyclone separator and are collected by an electrostatic precipitator (ESP). The Ecat from residual oil cracking units (ROCU Ecat) alone amounts to 6–9 tons/day [2] while the EPcat accounts for 200–300 kg/day. Furimsky [3] pointed out that about 400,000 tons of FCCU waste catalysts were produced annually. As for the possible alternatives of reusing these waste catalysts, Hsu

Table 1
Chemical composition of ROCU waste catalysts (unit: %)

Catalyst type	Component								
	LOI ^a	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
ROCU Ecat	3.31	51.69	41.12	1.08	1.73	0.41	0.48	0.42	0.06
ROCU EPcat	7.57	45.06	32.91	3.04	2.30	1.10	8.09	0.37	0.06

^a LOI: loss on ignition.

* Corresponding author. Tel.: +886-5-534-4140; fax: +886-5-537-1703.

E-mail address: sun@pine.yuntech.edu.tw (N. Su).

Table 2
Element analysis of waste catalyst using SEM–EDS (unit: %)

Catalyst type	Element									
	Mg	Al	Si	K	Fe	Ti	S	V	Ni	O
ROCU	0.73	21.95	24.73	ND	1.16	0.63	0.20	0.47	0.42	49.71
Ecat										
ROCU	1.01	17.25	23.12	ND	2.17	0.56	4.32	0.48	0.70	50.38
EPcat										

et al. [4] reported that waste catalysts from ROCU can stand heat of more than 1750°C. Therefore, it can be used for manufacturing fire-proof materials, or 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 of volatile organic compounds (VOCs) manufactured from recycled ROCU and FCCU waste catalysts was reported to be one-third that of activated charcoal [5]. Lin et al. [6] reported that the hardness of asphalt concrete could be greatly improved by combining industrial fly ash, particulates from bag filter, and waste catalysts in different proportions. In his review of spent refinery catalysts, Furimsky [3] concluded that the best way to recycle waste catalysts is to utilize it for concrete mixing. These so-called wastes are in fact of great value to the concrete industry. For Portland cement that is produced from the reaction of limestone and clay in a high-temperature rotary kiln, waste catalysts can make up 6% of the cementitious raw materials with the rest being 75% limestone and 19% clay.

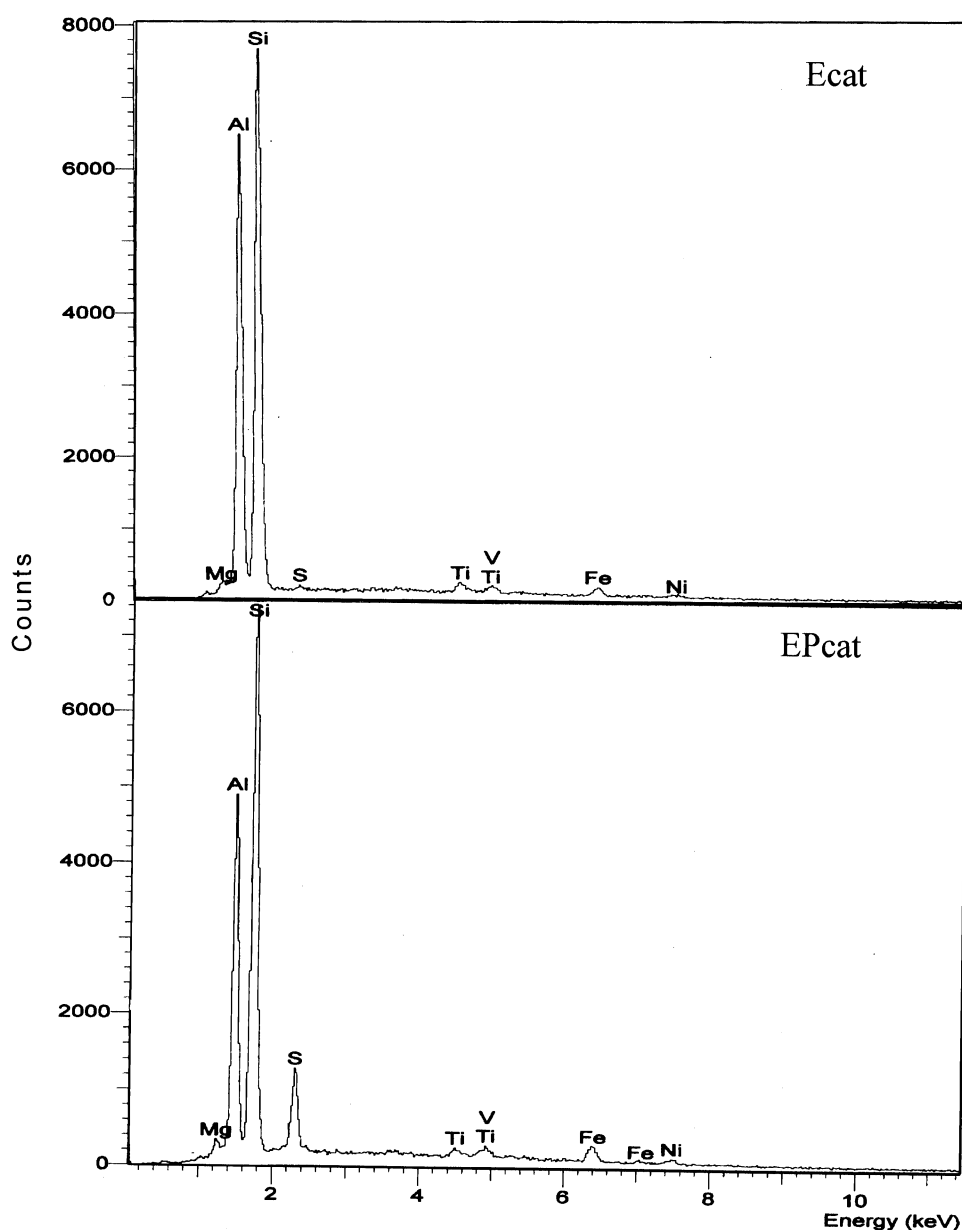


Fig. 1. EDS analysis of ROCU waste catalysts.

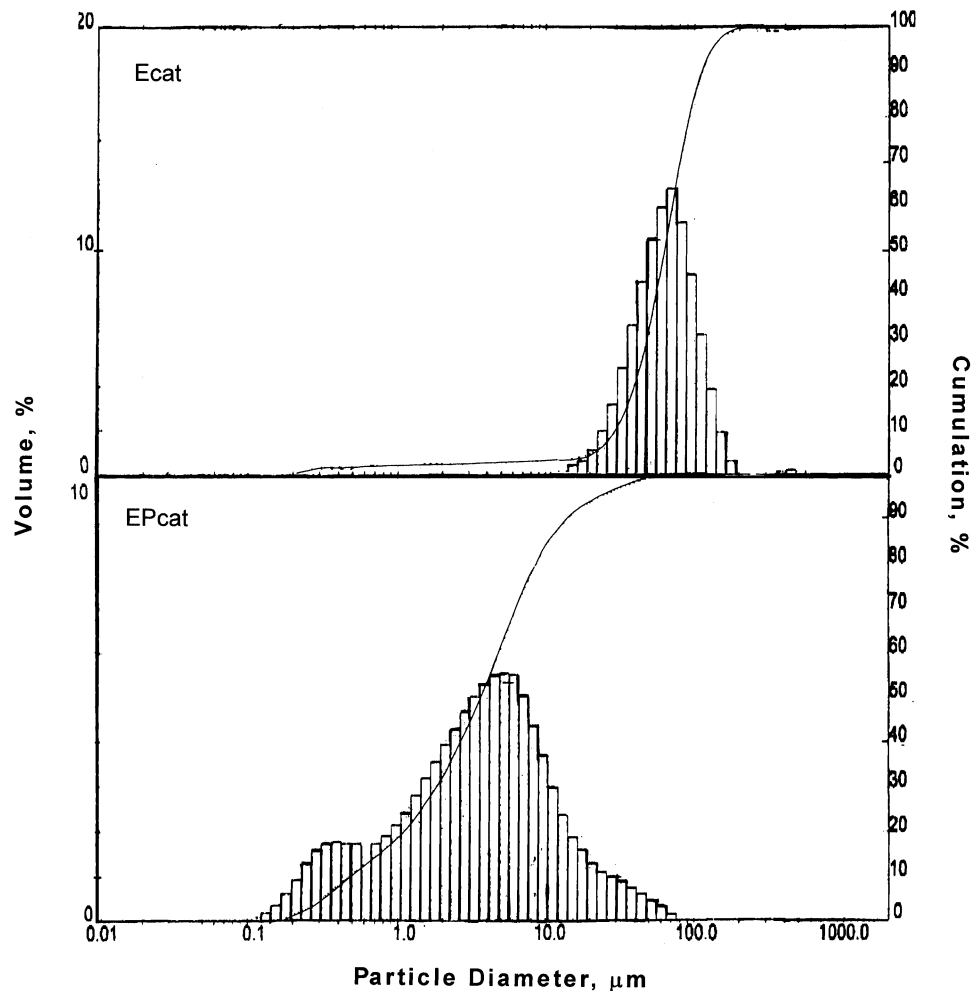


Fig. 2. Size distribution of ROCU waste catalysts.

Tests performed on these waste catalysts revealed that they are not hazardous. Schmit [3] pointed out that waste catalysts were used for manufacturing bricks. Comprising 5% of waste catalysts, these bricks were proven to be environmentally safe. Escardino et al. [3] compared the ceramic products made materials using FCCU waste catalysts and those made from kaolin with some other materials. These products were all found to have the same quality.

Most researches [7–12] on recycling Ecat dealt with extraction of useful metals to be reused for making new catalysts. They are also taken as raw materials for manufacturing cement, ceramics, bricks, or tiles. After repeated use, they are finally mixed with cement and buried in landfills. In the past, large quantities of EPcat escaped through the chimneys, resulting in serious air pollution. Although this environmental hazard is now solved by the installation of the ESP, the waste catalysts thus collected are causing another type of problem. Studies on the management of waste catalysts have been scarce [3]. So far, the solution to this problem is to bury it underground. This research aims at investigating an alternative way to reuse

Ecat and EPcat, and assessing the impact of their use on the environment. In this study, instead of adding these waste catalysts to the cement in the kiln, we added them to the mortar to substitute part of the cement required in the grout mixer. The physical properties of the substituted mortar and the feasibility of using this mortar as a construction material are investigated.

2. Experimental design

2.1. Materials

2.1.1. Cement

Type I Portland cement from Taiwan Cement was used in this study. Its specific gravity is 3.15. Its physical and chemical properties meet the requirements of ASTM C150.

2.1.2. Sand

Standard sand from Ottawa, US, that meets the requirements of ASTM C778 was used.

Table 3
Water content and pH of ROCU waste catalysts

Analysis	Catalyst type	
	ROCU Ecat	ROCU EPcat
Water content (%)	0.4	4.6
pH of waste in water	4.52	3.82

2.1.3. Waste catalyst

The waste catalysts came from the plant of China Petroleum in Ta-Lin, Taiwan.

2.2. Methods

The proportion of cement substitution in this experiment included 5%, 10%, and 15%, with 0% substitution being the control group. The W/C ratios were 0.42, 0.485, and 0.55 while the cement to sand ratio was 1:2.75.

The following experiments were conducted.

2.2.1. Analysis of the basic properties of waste catalysts

Component analysis, SEM–EDS element and compound analysis, size distribution and sieve analysis of particulates, apparent bulk density, and specific gravity, BET surface area, observation of microstructure, X-ray diffraction analysis, and analysis of total quantity of heavy metals.

2.2.2. Fresh mortar

Fluidity test, bleeding content test, setting time test, and hydration heat test [13].

2.2.3. Hardened mortar

Compressive strength test, water absorptivity test, X-ray diffraction analysis, toxicity characteristic leaching procedure (TCLP), and microscopic analysis [13].

3. Results and discussion

3.1. Basic properties of waste catalysts

3.1.1. Chemical composition

Table 1 shows the chemical composition of ROCU waste catalysts. Wet chemistry analysis revealed that they

Table 4
Bulk density, specific gravity, and BET surface area of ROCU waste catalysts

Catalyst type	Analysis		
	Apparent bulk density (g/cm ³)	Specific gravity	BET surface area (m ² /g)
ROCU Ecat	0.88	2.48	249.65
ROCU EPcat	—	2.34	98.77

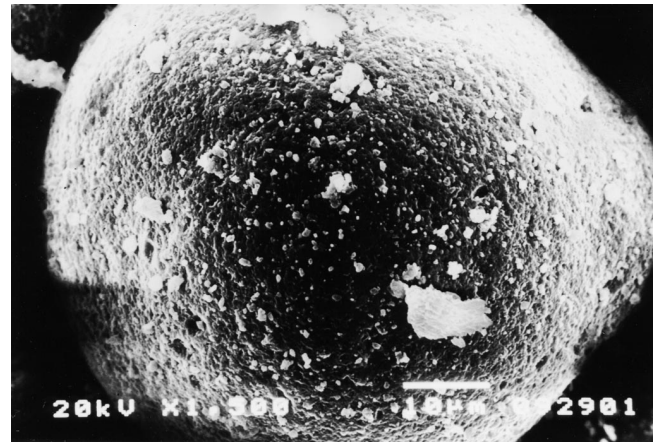


Fig. 3. Micrograph of ROCU Ecat ($\times 1500$) under SEM.

are mainly made up of SiO_2 and Al_2O_3 . As can be seen, these two components account for over 90% and 75% of the total weight in Ecat and EPcat, respectively. Hsu et al. [4] reported that 80% of ROCU waste catalysts were SiO_2 and Al_2O_3 , while Furimsky [3] reported that FCCU Ecat contained 60 wt.% of SiO_2 and 40 wt.% Al_2O_3 together with some other impurities of minute quantities. In addition, the chemical compositions of Ecat and EPcat are similar. However, EPcat contains more SO_3 (8.09%) than Ecat (0.48%). This may be caused by the fact that EPcat passes through the chimney before being captured by the ESP.

3.1.2. SEM–EDS element analysis

Results of element analysis with SEM–EDS are shown in Table 2 and Fig. 1. The main elements are found to be Si, Al, and O; with the rest being Mg, K, Fe, Ti, S, V, and Ni. Sadeghbeigi [14] pointed out that crude oil contains Ni, V, and alkali metals. Hence, the Ni, V, and S in the catalyst probably come from crude oil. The presence of Fe in the

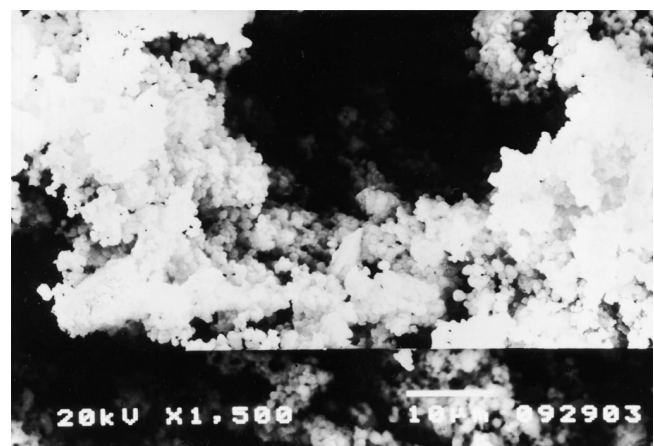


Fig. 4. Micrograph of ROCU EPcat ($\times 1500$) under SEM.

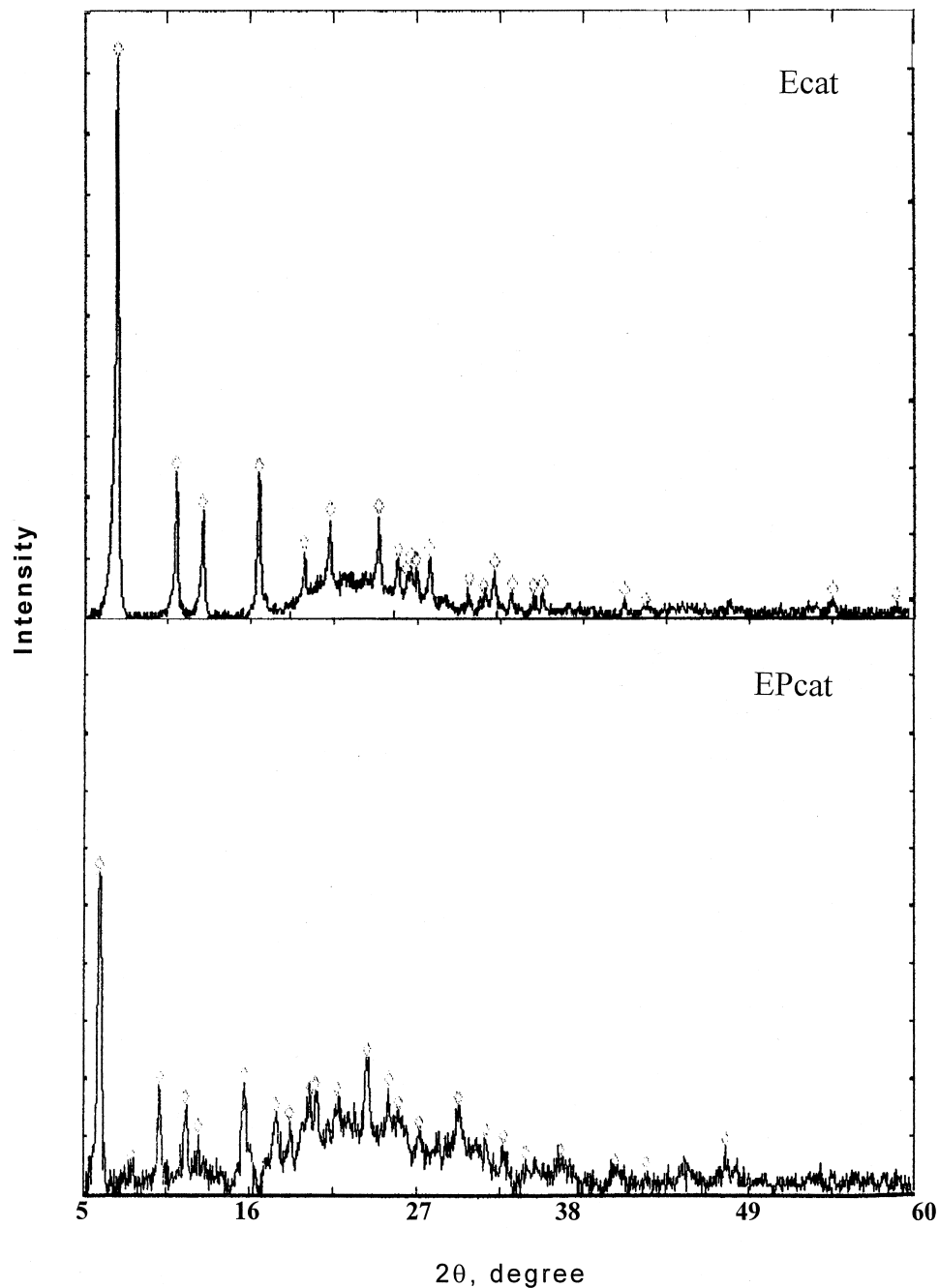


Fig. 5. X-ray diffractions of ROCU waste catalysts.

catalyst may result from the oxidation of the equipment. In general, EPcat contains more metals than Ecat.

3.1.3. Size distribution analysis and sieve analysis

As seen in Fig. 2, the particle size of ROCU Ecat is 37–100 μm with an average diameter of 68.52 μm . The size of EPcat is much smaller, with an average diameter of only 6.37 μm , which is about one-tenth that of Ecat. Therefore, Ecat looks granular while EPcat appears powdery. Fig. 2 also shows that the size distribution of Ecat is narrower than that of EPcat, which ranges from 0.1 to 100 μm .

3.1.4. Water content and pH value

EPcat contains more water than Ecat (Table 3). Chang et al. [5] pointed out that waste catalysts obtained from both ROCU and FCCU are acidic. However, EPcat is more acidic than Ecat because EPcat contains more sulfur than Ecat. The sulfur in EPcat reacts with water to form sulfuric acid in the chimney resulting in a decrease in the pH value.

3.1.5. Bulk density, specific gravity, and BET surface area

EPcat has slightly lower specific gravity than Ecat. In general, BET surface area greater than 1 m^2/g is consi-

Table 5
TCLP analysis of ROCU waste catalysts (unit: mg/l)

Catalyst type	Metal component		
	Cd	Cr	Pb
ROCU Ecat	0.000	0.0692	0.1261
ROCU EPcat	0.0601	0.8880	1.469
Regulatory standard	1.0	5.0	5.0

dered very large. Since zeolite catalysts are porous, their BET surface area is quite large (Table 4). The BET surface area of Ecat is about three times that of EPcat. This is probably due to the particle size and pore structure of waste catalysts.

3.1.6. Microstructure observation

Micrographs of ROCU Ecat and EPcat under SEM are shown in Figs. 3 and 4, respectively. These images were magnified 1500 times. It can be seen that Ecat is coarse, porous, and spherical, hence it should have a large BET surface area. Liu [15] reported that the surface of Ecat is very coarse, thus making it ideal for catalytic cracking reaction. When magnified 10,000 times, the result shows that Ecat is made up of many tiny catalyst particles sintered or agglomerated together. This implies that granulation is involved in the formation of Ecat. When ROCU EPcat is magnified 1500 times, the image shows lots of powder stuck together. Images magnified 10,000 times reveal that EPcat is made up of spherical particles.

3.1.7. X-ray diffraction analysis

Fig. 5 illustrates the X-ray diffraction plots of ROCU Ecat and EPcat. Both catalysts have similar crystal structures close to that of Faujasite (sodium aluminate silicate hydrate, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4.7\text{SiO}_2 \cdot x\text{H}_2\text{O}$).

3.1.8. TCLP analysis

The toxicity leached from the ROCU catalysts was assessed according to the TCLP put forth by the Environmental Protection Agency (EPA) of Taiwan. As seen in Table 5, the amounts of heavy metals leached from both

Table 6
Fluidity value of mortar with partial cement substitution

Item	Cement substituted (%)	W/C		
		0.42	0.485	0.55
ROCU Ecat	0	42.5	60.0	115.0
	5	42.5	60.0	92.5
	10	40.0	57.5	91.0
	15	37.5	57.5	90.0
ROCU EPcat	0	42.5	60.0	115.0
	5	37.5	60.0	101.0
	10	37.5	55.0	87.5
	15	0	37.5	65.0

Table 7
Bleeding content of mortar with cement partially substituted by ROCU Ecat

W/C	Item	Substitution			
		0%	5%	10%	15%
0.55	Bleeding content (%)	13.08	12.11	11.49	6.59
	Unit area bleeding (cc/cm^2)	0.333	0.283	0.305	0.164
0.485	Bleeding content (%)	5.35	1.77	1.52	0
	Unit area bleeding (cc/cm^2)	0.123	0.035	0.043	0
0.42	Bleeding content (%)	0.92	0	0	0
	Unit area bleeding (cc/cm^2)	0.020	0	0	0

Ecat and EPcat were in low concentration and met the regulatory standards ($\text{Cd} < 1 \text{ mg/l}$, $\text{Cr} < 5 \text{ mg/l}$, $\text{Pb} < 5 \text{ mg/l}$). Therefore, they are non-hazardous and can be classified as general industrial wastes. As a whole, EPcat leached more heavy metals than Ecat. It occurs probably because the particle size of EPcat is far smaller than that of Ecat. In addition, EPcat can be obtained from Ecat by size reduction. Structural destruction will result in greater leaching of the heavy metal components.

3.2. Recycling of ROCU waste catalysts

3.2.1. Characteristics of fresh mortar

3.2.1.1. Fluidity test. Table 6 shows the fluidity value of mortar with part of its cement substituted by ROCU Ecat or EPcat. Fluidity value increased with higher W/C ratio, but decreased with greater percentage of cement substitution. Since waste catalysts are of porous structure, these materials have high water absorptivity, thus affecting the fluidity value of mortar samples.

3.2.1.2. Bleeding test. Similar to fluidity value, bleeding of mortar samples increased with higher W/C ratio, but decreased with greater percentage of cement substitution. As seen in Tables 7 and 8, bleeding in EPcat is less significant than that in Ecat, indicating that EPcat has higher water absorptivity than Ecat. Although EPcat itself contains more water than Ecat, it is smaller and lighter, thus accounting for a higher content in mortar than Ecat.

3.2.1.3. Setting time. Generally speaking, the more cement is substituted by waste catalysts, the shorter the setting time is. This is because the waste catalysts are porous and have

Table 8
Bleeding content of mortar with cement partially substituted by ROCU EPcat

W/C	Item	Substitution			
		0%	5%	10%	15%
0.55	Bleeding content (%)	12.93	8.35	2.14	0.25
	Unit area bleeding (cc/cm^2)	0.349	0.230	0.055	0.005
0.485	Bleeding content (%)	7.29	4.65	0.84	0
	Unit area bleeding (cc/cm^2)	0.159	0.102	0.021	0

large BET surface area. Therefore, water content is reduced as the percentage of cement substitution increases and thus shortens the setting time required.

3.2.1.4. Hydration heat. Fig. 6 illustrates the hydration heat of mortars when $W/C=0.42$. It can be seen that mortar with 5% substitution released the greatest hydration heat, implying that waste catalysts continued to release heat after hydration. Although less hydration heat is released in mortar with partial cement substitution, a 5% substitution is too small to offset the heat released by waste catalysts. Therefore, in the early stage, the strength of mortar with 5% substitution will be higher than that of mortar with 10% or 15% substitution.

3.2.2. Characteristics of hardened mortar

Three different water to cement ratios, i.e., $W/C=0.42$, 0.485, and 0.55, were studied. In order to minimize experimental error, the standard sand was used for formulation. The cement to sand ratio in the mortar is 1:2.75 (weight ratio). The mortar cubes of 0% to 15% substitution were cured in saturated lime water at 23°C for different time periods (age) before being tested.

3.2.2.1. Compressive strength. *Mortar substituted with Ecat, $W/C=0.55$.* As seen in Fig. 7, mortar with 5% substitution showed strength of 1–2 MPa higher than that of the unsubstituted mortar both after 7 and 56 days. Mortar with 10% substitution showed strength of 4 MPa lower than

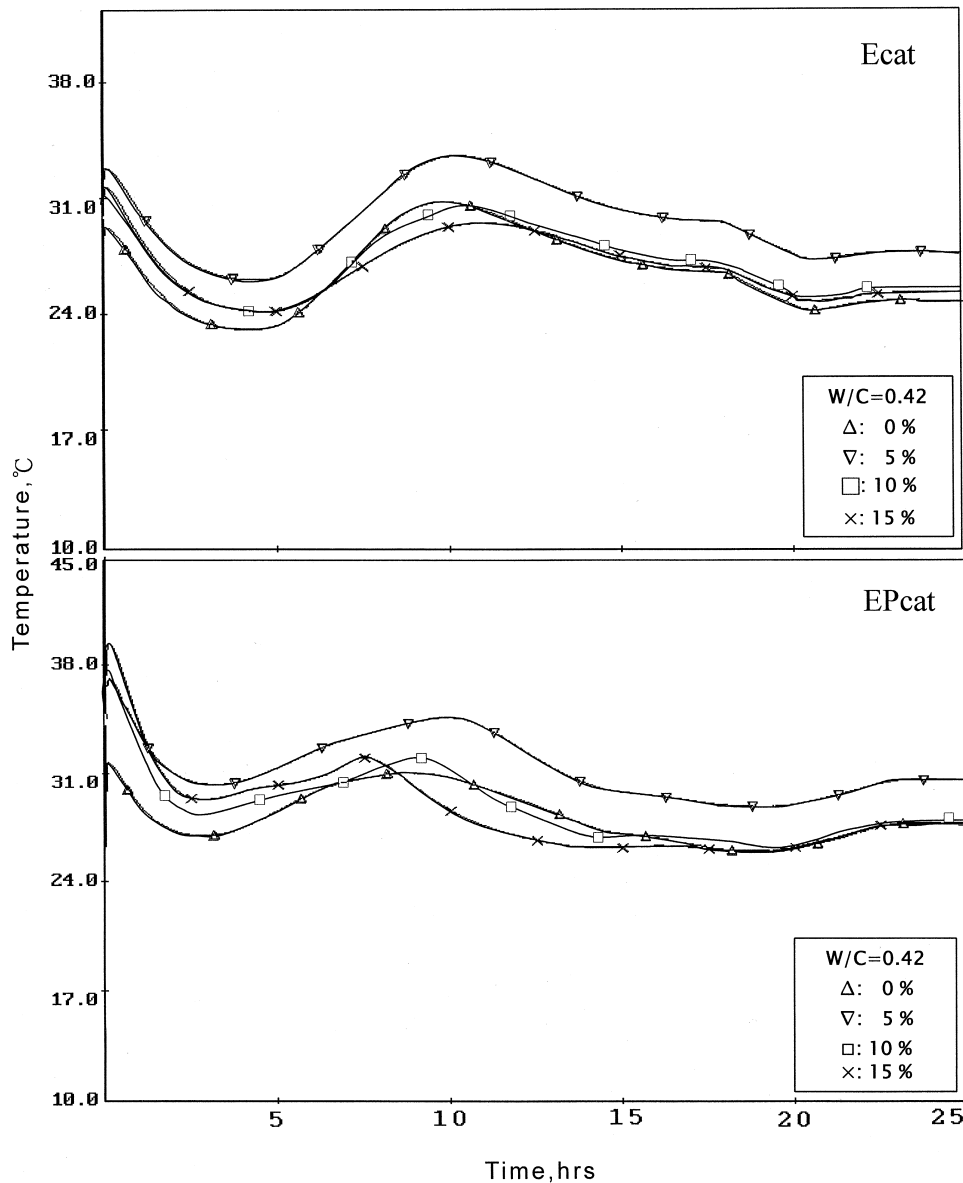


Fig. 6. Hydration heat of substituted mortar.

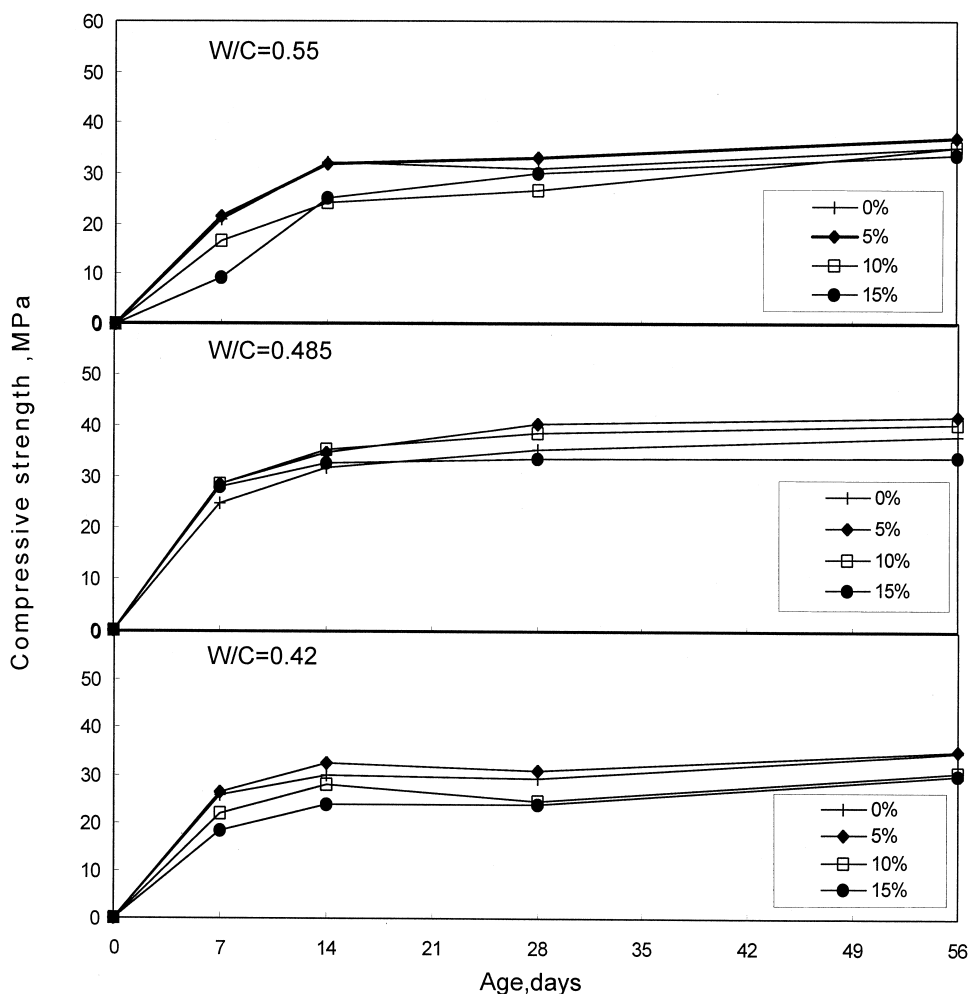


Fig. 7. Compressive strength of mortar substituted with Ecat.

that of the control group (unsubstituted mortar) after 7 days. However, the strength became close to that of the control group after 56 days. Similarly, mortar with 15% substitution showed low initial strength after 7 days but reasonable strength after 56 days.

Mortar substituted with Ecat, $W/C=0.485$. Mortar with 5% substitution has higher strength than the control group both after 7 and 56 days. Mortars with 10% and 15% substitution showed strength similar to that of the control group after 7 days. However, after 56 days, they showed strength of 9 MPa higher than that of the unsubstituted mortar. The increase in strength for mortar with 5% substitution is greater than mortars with 10% and 15% substitution after 14 days.

Mortar substituted with Ecat, $W/C=0.42$. Mortar with 5% substitution showed strength of 0.5 MPa higher than that of the control group after 7 and 56 days. Mortars with 10% and 15% substitution showed similar strength (~ 30 MPa) in the later stage. However, their strength was 5 MPa lower than that of the control group both after 7 and 56 days.

Mortar substituted with EPcat, $W/C=0.55$. As shown in Fig. 8, mortars with 5%, 10%, and 15% substitution showed an average strength of 3–4 MPa and 5–6 MPa higher than that of the control group at both early and later stages, respectively. Among the three types of substituted mortars, the one with 10% substitution showed the best compressive strength; while that with 15% substitution showed a sharp increase in strength after 14 days.

Mortar substituted with EPcat, $W/C=0.485$. Similarly, mortars with 5%, 10%, and 15% substitution showed an average strength of 5–6 MPa and 4–10 MPa higher than that of the control group at both early and later stages, respectively. Compressive strength increased with longer curing age and higher percent of substitution. All three types of substituted mortars showed similar strength at the early stage; while their compressive strength increased with increasing percentage of substitution.

Mortar substituted with EPcat, $W/C=0.42$. Mortars with 5% and 10% substitution showed an average strength of 4 MPa and 2–3 MPa higher than that of the control group at both early and later stages, respectively. Although mortar

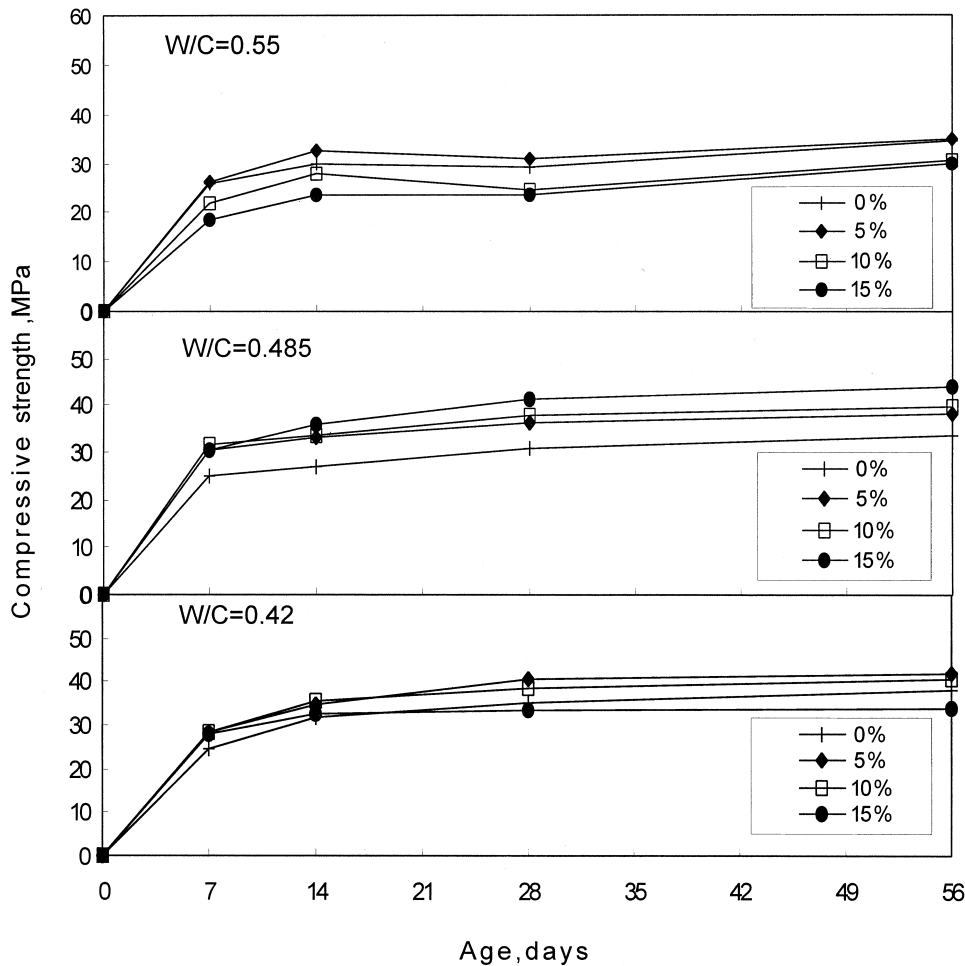


Fig. 8. Compressive strength of mortar substituted with EPcat.

with 15% substitution also had higher initial strength than the control group, its strength became 4 MPa lower than that of the unsubstituted mortar at the later stage. This is probably due to insufficient amount of water used for mixing.

3.2.2.2. Water absorption rate. Water absorption rate has been used as an indication for porosity and swelling behavior of mortar [16]. Water absorption rate of mortars substituted with Ecat increased with longer curing age as well as higher percentage of substitution. Comparatively, mortar substituted with EPcat had lower water absorption than that substituted with Ecat. At different W/C ratios, mortars with 5% and 10% substitution had almost the same water absorption rate as the control group; while the water absorption rate of mortar with 15% substitution was higher than the control group. As waste catalysts are porous, the mortar with higher percentage of substitution will have higher water absorption rate.

3.2.2.3. X-ray diffraction analysis. X-ray diffraction analysis was carried out on ROCU Ecat (curing age = 28 days,

W/C = 0.485) in order to study its crystal structure. The crystals of mortars of different percent of cement substitution were similar in composition. These crystals contained SiO_2 (quartz), CaO , CaCO_3 (calcite), and $\text{CaSiO}_4 \cdot 0.3\text{H}_2\text{O}$.

3.2.2.4. TCLP analysis. Tables 9 and 10 show the results of the TCLP analysis. As can be seen, the concentrations of TCLP leached from mortars with 5–15% cement substitution by Ecat or EPcat were all lower than the regulatory standard for hazardous substance. They also met the regulatory effluent standard. The TCLP test result of hardened

Table 9
TCLP analysis on mortar substituted with ROCU Ecat (unit: mg/l)

Cement substituted	Heavy metal component		
	Cd	Cr	Pb
0%	ND	0.139	0.028
5%	ND	0.209	0.060
10%	ND	0.185	0.046
15%	ND	0.209	0.046
Regulatory standard	1.0	5.0	5.0

ND: not detected.

Table 10
TCLP analysis on mortar substituted with ROCU EPcat (unit: mg/l)

Cement substitution (%)	Heavy metal component		
	Cd	Cr	Pb
0%			
5%	ND	0.209	0.004
10%	ND	0.232	0.004
15%	ND	0.185	0.014
Regulatory standard	1.0	5.0	5.0

ND: not detected.

concrete was lower than that of fresh concrete. Sun et al. [17] pointed out that the encapsulation of waste FCCU catalyst by Portland cement could reach 60 wt.% and still retain good stability. Van Eijk and Brouwers [18] reported that the heavy metal leaching rate was greatly affected by the composition of cement, especially the amount of $\text{Ca}(\text{OH})_2$ present. An optimum $\text{Ca}(\text{OH})_2$ content would show the maximum inhibition of heavy metal leaching. Leaching was also a function of porosity, degree of hydration or water to cement ratio. When pollutants were released from the acidic water, the presence of $\text{Ca}(\text{OH})_2$ would slow down the release rate. On the other hand, if $\text{Ca}(\text{OH})_2$ become dissolved, it would leave extra pores on the body that would accelerate dissolution of the main body. For example, at pH 4.6, $\text{Ca}(\text{OH})_2$ will dissolve totally, accounting for 68% of calcium present in calcium-silicate-hydrate (C-S-H) [18].

4. Conclusions

This study analyzes the basic chemical properties of ROCU waste catalysts, Ecat and EPcat. The feasibility of reusing them for cement substitution in mortar preparation is investigated. A summary of our findings is as follows.

1. Observation of ROCU waste catalysts with SEM reveals that they are of porous structure, with a significantly large BET surface area. They are mainly composed of SiO_2 and Al_2O_3 .
2. ROCU Ecat and EPcat have very similar chemical composition and physical properties except that EPcat contains more heavy metals than Ecat.
3. TCLP analysis proves that these two waste catalysts are non-hazardous and can thus be classified as general industrial waste. In addition, recycling these catalysts would not result in further environmental pollution.
4. The Fluidity value of mortar substituted with Ecat or EPcat increases with higher W/C ratio, but decreased with greater percent of substitution.
5. Similarly, bleeding of mortar substituted with Ecat or EPcat increases with higher W/C ratio, but decreases with greater percentage of substitution.
6. Mortar with 5% substitution by waste catalysts shows the highest heat release. Hence, mortar with 5% substitution would have higher strength at the early stage. Hydration

reaction of waste catalyst is different from that of fly ash as the latter does not release or absorb heat.

7. When W/C=0.55, mortar with 5% ROCU Ecat substitution shows higher compressive strength than the unsubstituted control group. Mortar with 10% substitution has initial strength lower than that of the control group; however, its strength increases at the later stage, coming close to that of the control group. When W/C=0.485, the substituted mortars are far better than the substituted control. When W/C=0.42, mortar with 5% substitution shows higher strength than the control group.

8. When W/C=0.55, for mortar substituted with ROCU EPcat, the percent of substitution can be as high as 15% and it still shows better compressive strength than the control group. Similarly, when W/C=0.485, substitution can also be as high as 15% without imparting any adverse effect on strength. When W/C=0.42, substitution up to 10% still shows better compressive strength. However, if it is increased to 15%, the strength will become lower than that of the control group.

9. Mortars substituted with EPcat at 5–15% all show higher strength than those substituted with Ecat. This is probably because EPcat particles are much smaller than Ecat particles; thus they are better distributed in mortar than Ecat particles.

10. Observation of the crystal structure reveals that all mortars with partial substitution by waste catalysts have similar crystal compositions, which contains SiO_2 (quartz), CaO , CaCO_3 (calcite), and $\text{CaSiO}_4 \cdot 0.3\text{H}_2\text{O}$.

12. These waste catalysts can absorb water easily, thus reducing the W/C ratio in the liquid phase of the mortar. As a result, the W/C ratio of hardened mortar is lower than the apparent W/C ratio. When the percent of cement substitution by waste catalysts is not very high, its strength at the early stage is higher than that of the control group. Therefore, we conclude that a decrease in the W/C ratio is beneficial to the concrete strength at the later stage.

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