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Evaluation of Sintering Characteristics of Pavement Tiles Incorporating Waste Catalyst

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Abstract: This investigation elucidates the sintering characteristics of pavement tile made from a blend with waste catalyst to evaluate the feasibility of the reuse of the waste catalyst. The following operating conditions were adopted; pressing pressure 25*kgf/cm*^{2}, sintering temperature from 900 to 1200°C, sintering time 6hrs, waste catalyst percentage by weight from 0 to 50%, and heating rate of 5°C/*min*. The water absorption and porosity increases with the amount of waste catalyst added to the mixture. Increasing the amount of waste catalyst in the pavement tiles reduces the ignition. The hardness test results show that the hardness of the clay and waste catalyst pavement tiles depends strongly on the amount of waste catalyst present in the pavement tile and the heating temperature. The correlation between the water absorption and the porosity ratio demonstrates that the water absorption rate increases with the porosity. The effects of sintering temperature and the quantity (%) of the waste catalyst mixed with clay on the properties of the prepared pavement tiles are reported.

Key words: *Absorption rate; Bulk density; Pavement tile; Porosity ratio; Waste catalyst.*

Introduction

Large quantities of catalysts have been used in the refining industry to purify and upgrade various petroleum products and residues, which in turn have generated a significant amount of waste catalysts. The catalytic reactions of the fluid catalytic cracking unit (FCCU) process generate two waste catalysts. One is the equilibrium catalyst (Ecat), which must be replaced to retain its catalytic activity. The other is named the electrostatic precipitator catalyst (EPcat) [1]. EPcat can be collected from the cyclone separator using an electrostatic precipitator (ESP). The amount of Ecat that comes from residual oil cracking units (ROCU Ecat) alone is 6 to 9*tons/day* while EPcat accounts for 200 to 300*kg/day* in Taiwan [2, 3].

The volume of waste hydroprocessing catalysts discarded as solid wastes has increased significantly following a steady increase in the processing of heavier feedstocks that contain more sulfur, nitrogen, and metal, along with a rapid growth in the distillate hydroprocessing capacity that has been installed to meet the increasing demand for low-sulfur fuels [4]. Chemicals present in waste catalysts, such as V, Ni, Mo, and Co, can be leached out by water during disposal, polluting the environment [4]. Accordingly, the disposal of these hazardous wastes in landfills commonly contaminates the ground water, detrimentally affecting the biota [5]. The hazardous nature of the waste catalysts has already drawn attention from environmental authorities in numerous countries and industries are pressured from such authorities to improve their handling of waste catalysts.

The main components of waste catalysts are silica, aluminum, and calcium. Many alternative approaches can be used to handle the spent catalyst by refiners, including disposal in landfills; reclamation of metals; regeneration/rejuvenation and reuse; utilization as raw materials to generated fine aggregate [3]; use as pozzolanic material [2], ceramic frits [6], and glass–ceramic [7], etc. Furthermore, while the main components of waste catalysts are similar to sewage sludge, Lin et al. [8] replaced part of clay by sewage sludge ash to manufacture tiles. The effects of quantities of sludge ash, amount of nano-SiO_2 added, and kiln temperatures on the properties of tile were studied. They observed that the strength of sludge ash tile can be improved by the addition of nano-SiO_2 additive and it is feasible to apply sludge ash as part of raw material to make tile. However, the kiln temperature should be carefully considered when nano-SiO_2 is applied to sludge ash tiles. Yet again, in order to see how the properties of sludge ash tiles can be improved by glazes, Lin et al. [9] applied four colorants, Fe_2O_3 (red), V_2O_5 (yellow), $CoCO_3$ (blue), and MnO_2 (purple) with four different glaze concentrations on sludge ash biscuit tile specimens. They noticed that mechanical properties such as water absorption, bending strength, and abrasion were improved with the application of glazes. Moreover, red glazed tiles showed the most stable performance, followed by blue, yellow, and purple.

In Taiwan, since there are needs for pavement tile used in the construction of parking lot either for decorations or engineering applications, the objective of this study was to evaluate the best ways of using waste catalysts as materials in producing pavement tiles. The following operating conditions were utilized in this study: pressing pressure of 25*kgf/cm*^{2}; sintering temperature of 900 to 1200°C; sintering time of 6hrs; percentage of waste catalysts varying from 0 to 50% by weight; and heating rate of 5°C/*min*. In this study, the waste catalysts were blended with clay to produce tile samples. The sintering characteristics, including shrinkage, weight loss on ignition, water absorption, bulk density, hardness, and mineralogical composition were also evaluated.

Materials and Evaluation Methods

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Table 1. Chemical Compositions and Total Metals of Clay and Waste Catalyst.

Composition	Clay	Waste Catalyst
SiO_2 (%)	61.5	39
Al_2O_3 (%)	15.84	59
Fe_2O_3* (%)	6.11	N.D.
CaO (%)	0.36	0.1
K_2O (%)	2.73	0.01
Cu (*mg/kg*)	4	9.6
Zn (*mg/kg*)	28	46.8
Pb* (*mg/kg*)	N.D.	21.5
Cr (*mg/kg*)	6.02	9.8
Cd** (*mg/kg*)	N.D.	0.2

* $Fe_2O_3<0.014$*mg/kg*; $Pb<0.016$*mg/kg*; **$Cd<0.014$*mg/kg*.

Materials

The waste catalyst was obtained from the Refinery Business Division of Chinese Petroleum Corporation in Taiwan. Both waste catalyst and white clay were crushed to uniform particle sizes. The crushed materials were then ground until they could pass through a 16 mesh sieve and finally were oven dried. The chemical compositions of the raw materials were analyzed by X-ray fluorescence (XRF) and the results are shown in Table 1.

Experimental Procedures

In order to investigate the feasibility of reusing waste catalyst to make pavement tiles, the waste catalyst content in the clay-waste catalyst mixture was varied from 0 to 50% by weight. The mixture was then homogenized in a blender and pressure molded at 25kg/cm^2 to form a sample bar of 40×45×6*mm* in length, width, and height, respectively.

The specimens were air-dried at room temperature for 24hrs, followed by oven dried at 80°C for 24hrs to remove the water content. The dried specimens were then heated to a target temperature of 900, 1000, 1100, or 1200°C, with a heating rate of 5°C/*min*. After maintaining the target temperature for 6hrs, the samples were cooled to room temperature.

Analysis Methods

The physical characteristics of the tile, namely, the loss on ignition, firing shrinkage, water absorption, density, and hardness were analyzed and the toxicity characteristic leaching procedure was carried out. The following sections describe the testing procedures and calculation of the characteristics.

- Weight loss on ignition (LOI):
  LOI (%)= $(W_0-W_1)/W_0$x100%,
  where:
  W_0 and W_1= weight of the samples before and after sintering, respectively.
- Water absorption - Water absorption is calculated as the amount of water absorbed by tile after immersion in water for 24hrs:
  Water absorption (%) = $(W_0-W_1)/W_0$ x100%,
  where W_0 and W_1= weights of the samples before and after the immersion, respectively.
- Porosity ratio:
  Porosity ratio (%) = $(W_0-W_1)/(W_0-W_2)$
  where:
  W_0 = weight of saturated samples after the immersion in air,
  W_1= weight of samples before sintering,
  W_2 = weight of saturated samples after immersion in water.
- The crystalline phases of the heat-treated samples and the untreated ground mixture were all examined by X-ray diffraction (XRD) analysis. The mineralogy was determined by XRD analysis carried out by a Siemens D-5000X-ray diffractometer with CuKα radiation.
- The chemical compositions were determined by X-ray fluorescence (XRF) performed with an automated RIX 2000 spectrometer. The specimens were prepared for XRF analysis by mixing 0.4*g* of the sample and 4*g* of 100 Spectroflux, at a dilution ratio of 1:10. Homogenized mixtures were placed in Pt–Au crucibles, and then treated for 1hr at 1000°C in an electrical furnace. The homogeneous melted sample was recast into glass beads with 2 and 32*mm* in thickness and diameter, respectively.
- Toxic characteristic leaching procedure (TCLP), regulated by US EPA SW 846-1311 method: The extraction procedure required a preliminary evaluation of the pH characteristic of the sample to determine the proper extraction fluid necessary for the experiments. Upon testing, extraction fluid #B (pH 2.88±0.05) was used for the TCLP analysis. The fluid was prepared by adding 5.7*mL* of acetic acid to 500*mL* of double distilled water, diluted to a volume of 1*L*. A 25-*g* sample was placed in a 1-*L* Erlenmeyer flask and 500-*mL* of extraction fluid was added to each Erlenmeyer flask. These samples were agitated for 18hrs using an electric vibrator. The slurry produced was filtered with 6 to 8μm pore size Millipore filter paper. The leachates were preserved in 2% HNO_3 solution.
- Leaching concentrations: Cd (US EPA SW846-7131A), Pb (US EPA SW846-7421), Zn (US EPA SW846-7951), Cu (US EPA SW846-7211), and Cr (US EPA SW846-7191).
- Particle size distribution is determined by sieve analysis, CNS 486.

Results and Discussion

Characteristics of Clay and Waste Catalyst

Fig. 1 shows the particle size distribution of the clay and waste catalyst. The densities of the clay and waste catalyst are 2.43 and 2.4g/cm^3, respectively. The chemical compositions of the clay and waste catalyst were analyzed using XRF and the mineralogical composition was determined with X-ray diffraction. Table 1 shows the chemical compositions of the clay and waste catalyst. The clay had more SiO_2 and less Al_2O_3 than did the waste catalyst. The XRD analysis reveals that the principal constituents of the clay are quartz and Kaolinite, see Fig. 2. The waste catalyst is principally composed of silicon oxide with aluminum oxide and small amounts of calcium copper oxide ($CaCu_2O_3$), magnesium titanium oxide ($MgTi_2O_5$), cobalt titanium oxide ($CoTi_2O_5$), calcium zinc silicate ($Ca_2ZnSi_2O_7$), akermanite ($Ca_2MgSi_2O_7$), zinc silicate ($ZnSiO_3$), cobalt molybdenum

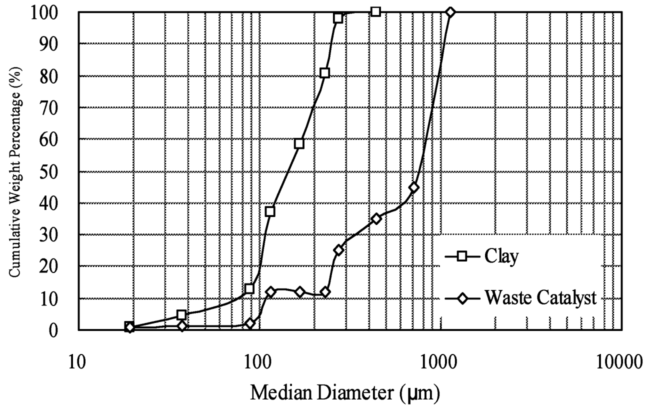


Fig. 1. Particle Size Distribution of the Clay and the Waste Catalyst.

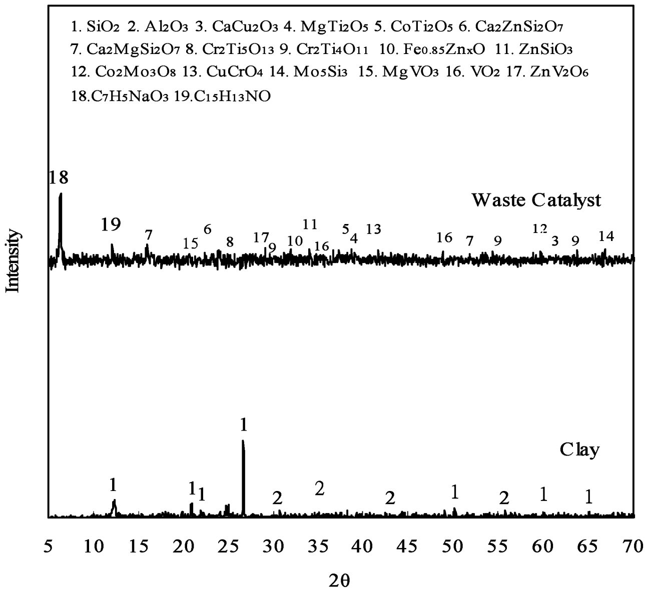


Fig. 2. XRD Patterns of the Clay and Waste Catalyst.

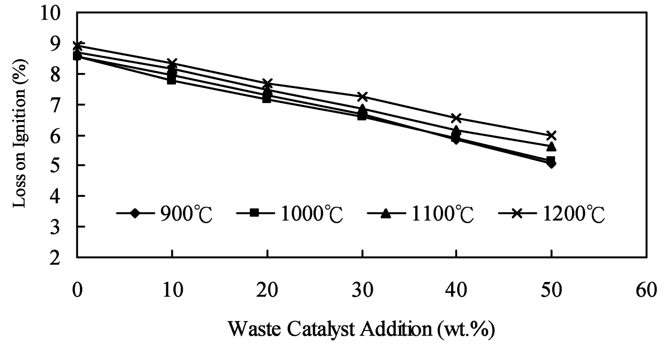


Fig. 3. Loss on Ignition of the Pavement Tiles.

oxide ($Co_2Mo_3O_8$), copper chromium oxide ($CuCrO_4$), molybdenum silicon (Mo_5Si_3), magnesium vanadium oxide ($MgVO_3$), vanadium oxide (VO_2), and zinc vanadium oxide (ZnV_2O_6).

As shown in Table 1, the metal contents of clay are 0.28*mg/kg* of Zn, 0.04*mg/kg* of Cu, and 0.06*mg/kg* of Cr. The metal contents of the waste catalyst are 46.8*mg/kg* of Zn, 21.5*mg/kg* of Pb, 9.8*mg/kg* of Cr, and 9.6*mg/kg* of Cu. The TCLP leaching concentrations of the clay and waste catalyst samples all met the ROC EPA's current regulatory thresholds (Table 2).

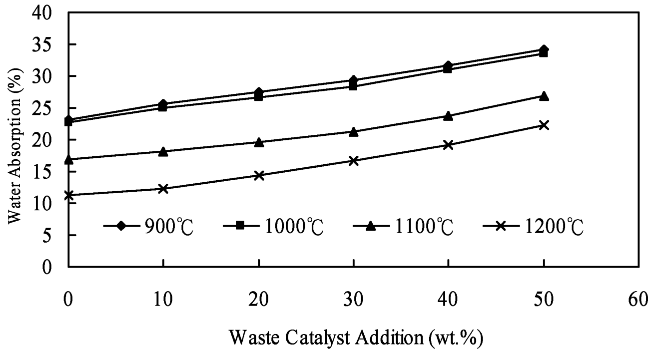


Fig. 4. Water Absorption of the Pavement Tiles.

Table 2. Leaching Concentrations of the Clay and Waste Catalyst.

Sample	Pb*	Cd**	Cr***	Cu****	Zn*****
Clay	N.D.	N.D.	N.D.	N.D.	0.12
Waste Catalyst	N.D.	N.D.	0.18	0.08	N.D.
Regulatory Limits (*mg/L*)	5.00	1.00	5.00	15.00	—

*Pb<0.016*mg/kg*; **Cd<0.014*mg/kg*; ***Cr<0.016*mg/kg*; ****Cu<0.016*mg/kg*; *****Zn<0.015*mg/kg*.

Loss on Ignition of Pavement Tiles

As shown in Fig. 3, the amounts of waste catalysts in the mixture varied from 0 to 50%; the shrinkages of pavement tiles were 8.91, 8.34, 7.67, 7.23, 6.56, and 5.96% for a heating temperature of 1200°C. In Fig. 3, it can be seen that decreasing the amounts of waste catalysts and increasing the temperature resulted in an increase in the weight loss on ignition. The weight loss on ignition of pavement tiles also depends on the amount of inorganic substances in both the clay, and the amount of waste catalyst burnt out during the sintering process. The addition of waste catalysts to the mixture caused an apparent decrease in the loss of weight. This was most likely due to the burning out of organic components during the sintering process. The loss of weight is possibly caused by water evolution, due to dehydroxylation of kaolinite, transforming to metakaolinite. There was a small weight loss at above 1000°C likely related to the formation of a Si-containing γ-Al_2O_3 with spinel structure and/or primary mullite [10, 11].

Water Absorption of Pavement Tiles

The water absorption is related to the volume of the open pores, e.g., pores connected with the specimen's surface. The water absorption is also closely related to densification of the specimens. Fig. 4 shows the water absorption results for pavement tile, with varying amounts of waste catalyst and heated at various temperatures. A comparison shows that increasing the amount of waste catalyst results in an increase in the water absorption, independent of the heating temperature. The water absorption of the pavement tile increases with an increase of waste catalyst content.

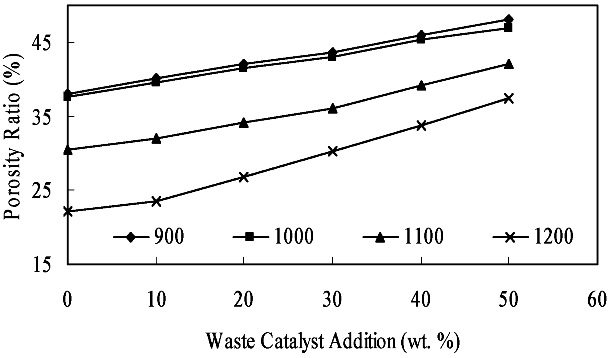


Fig. 5. Porosity of the Pavement Tiles.

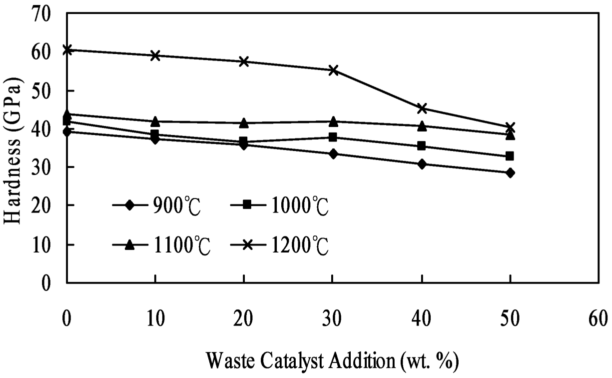


Fig. 6. Vickers Hardness of the Pavement Tiles.

It is probably due to the fact that, as sintering evolves the pores become rounded and smaller in the solid state sintering range, while, during the liquid phase sintering range, the pores are isolated from the outer surface and finally close. Sintering process accelerates at temperatures above 1100°C as the glassy phase is formed. In this phase, pores are penetrated, and then, closed becoming isolating from neighboring pores. This explains the intense decrease of water absorption in this temperature range.

Porosity of Pavement Tiles

Fig. 5 shows the effect of heating temperature on the porosity of pavement tiles made with various amounts of waste catalyst. As heating temperature increases the porosity ratio decreases, indicating enhanced densification. It can also be observed from Fig. 5 that, regardless of the replacement level of waste catalyst used, the increases in porosity ratio are significant. The higher porosity ratio of the pure clay pavement tiles at 900 and 1000°C is clearly visible, after which the porosity starts to decrease. At 1200°C, advanced sintering occurs at which the appearance of smaller pores can be observed. In this state, porosity has been reduced, which starts to negatively influence the dimensional stability of the porous pavement tiles and increase the linear shrinkage. The glassy viscous phase infiltrates the pores of the structure and causes densification by liquid phase sintering. The formation of kaolinite and feldspar can also cause densification. Therefore, it is expected that densification will increase with the increase in temperature.

Hardness of Pavement Tiles

The mechanical strength of the specimens was examined in terms of hardness, tested using the test method CNS 3299. The mechanical behavior was well correlated with all the other studied parameters. It is found that the Vickers hardness is sufficient for pavement tiles which require, in general, a hardness of 50*GPa*. The hardness of the pavement tiles is shown in Fig. 6. The samples sintered at 900°C had Vickers hardness between 30 and 40*GPa*. The Vickers hardness of samples with less than 30% waste catalyst sintered at 1200°C was very good, sufficiently high to satisfy the standard for pavement tiles according to CNS 3299. At 1200°C, the hardness decreased as the amount of waste catalyst increased. Compared to that of the control sample sintered at 1200°C, the clay with waste catalyst tile had decreasing hardness. It was also observed that the compressive strength increased with temperature as the sample become denser. It is known that porosity negatively influences strength. Pore closures can therefore result in an increase in hardness. This phenomenon was particularly clear at temperatures above 1100°C, as evidenced by the high densification level.

X-ray Diffraction Patterns of Pavement Tiles

Figs. 7 to 10 show the mineralogy of the pavement tiles after sintering. X-ray diffraction patterns of pavement tile samples sintered between 900 and 1200°C are shown in Figs. 7 to 10. It can be seen that samples with waste catalyst sintered at 900 and 1000°C, the dominant phases are quartz (SiO_2). At a temperature of 1100°C, in addition to quartz peaks, the characteristic peaks of kaolinite, feldspar, and $V_2Ti_3O_9$ can also be observed in the samples with waste catalyst (Fig. 9). When the temperature is increased to 1200°C, the $V_2Ti_3O_9$ peak intensities of the samples begin to increase and the quartz peak intensities begin to decrease. The amount of feldspar decreases at heating temperatures of 1100 and

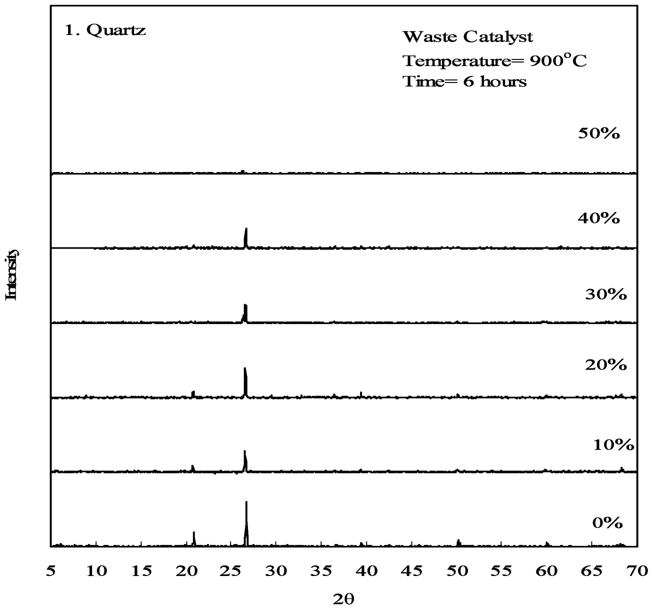


Fig. 7. X-ray Diffraction Patterns for Pavement Tiles Sintered at 900°C.

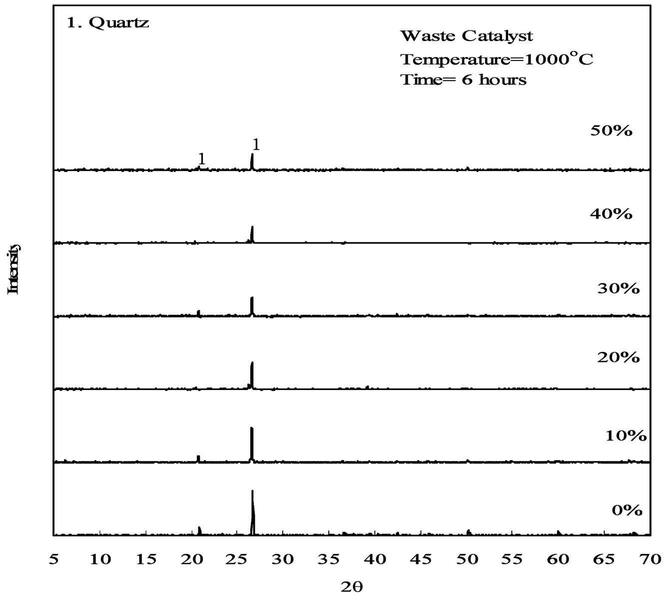


Fig. 8. X-ray Diffraction Patterns for Pavement Tiles Sintered at 1000°C.

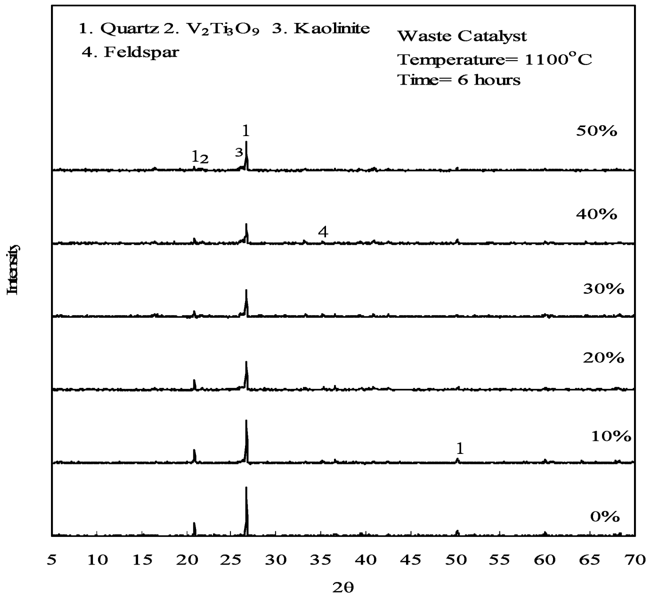


Fig. 9. X-ray Diffraction Patterns for Pavement Tiles Sintered at 1100°C.

1200°C [12, 13]. No mullite is present at 900°C. This is in agreement with the results of other investigators [14].

Microstructures of Pavement Tiles

Fig. 11 presents the microstructures of the pavement tiles containing 0 to 50% waste catalyst sintered at 1200°C. Fig. 11 (a) indicates that at 1200°C, the pure clay pavement tile structure was quite dense. The same is observed for tiles with 10% waste catalyst (Fig. 11 (b)). For tile samples containing more than 10% of waste catalyst, the porosity declines and the pore distribution was modified. Because of the sintered reaction between clay and waste catalyst, pavement tiles containing 10 to 50% waste catalyst surfaces were coarse,. In Fig. 11(f), it is clear that the amount and size of pores in the pavement tiles with 50% waste catalyst exceed those of the pure clay pavement tile.

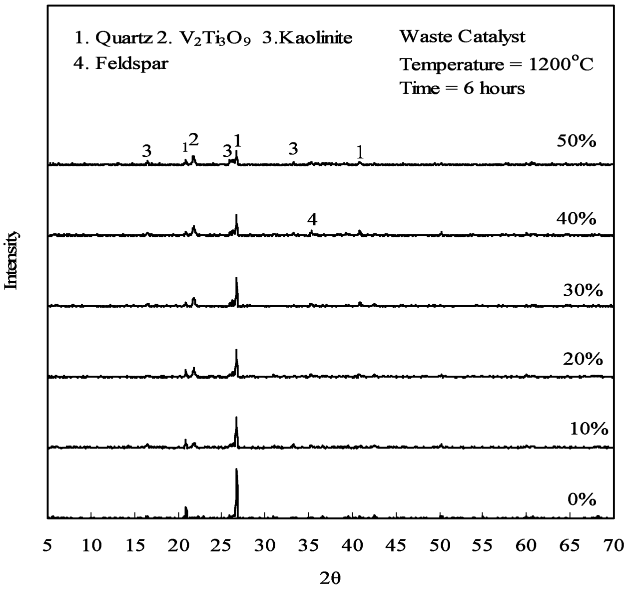


Fig. 10. X-ray Diffraction Patterns for Pavement Tiles Sintered at 1200°C.

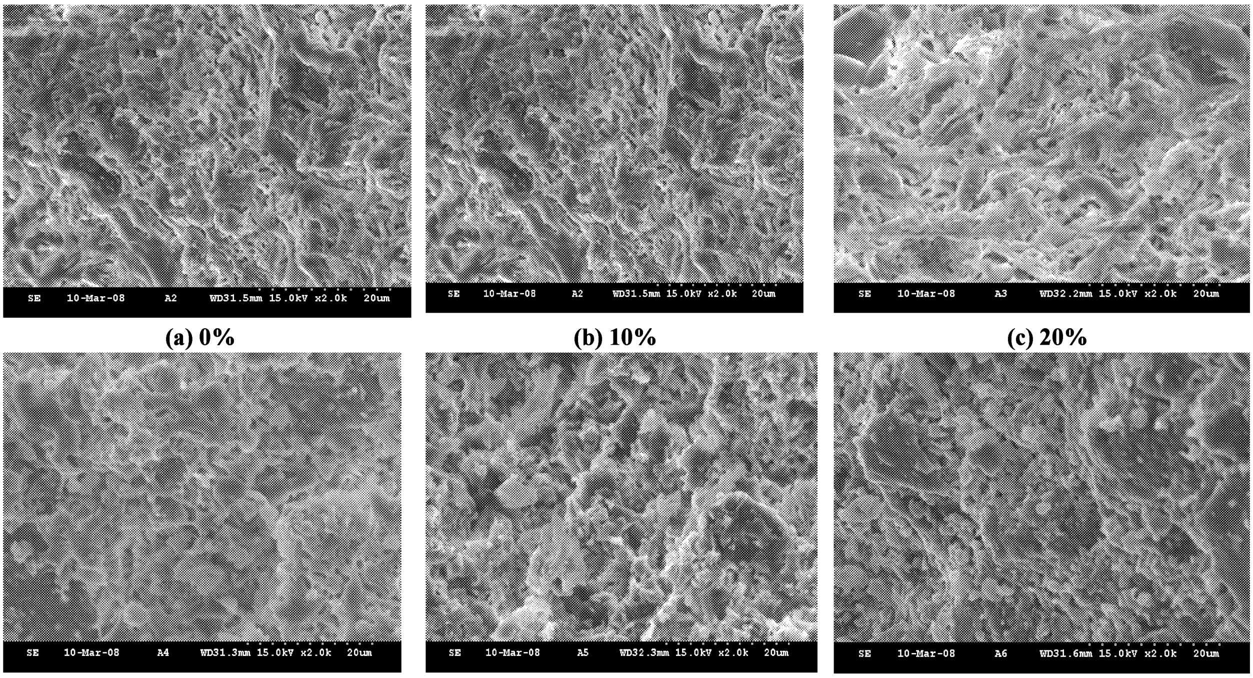
Relationships between Pavement Tile Properties

Relationships between various characteristics of the sample tiles and the porosity ratio are presented in Fig. 12. As shown in Fig. 12(a), density of the pavement tiles decreases almost linearly with increases of porosity ratio; with a coefficient of determination, R^2, of 0.95. Fig. 12(b) indicates that, in general, the percent shrinkage decreases as the porosity ratio increases; however, the trend is not apparent, with an R^2 of only 0.48. The relationship between the 24-hr water absorption and the porosity ratio is shown in Fig. 12(c) with an excellent R^2 value of 0.96. This may be due to the fact that the 24-hr water absorption is affected by the pores in the material. The 24-hr water absorption gives a measure of the pore space in the pavement tiles. Finally, Fig. 12(d) shows the relationship between the hardness and the porosity ratio for the pavement tiles used in the study. A linear relationship with an R^2 value of 0.79 was observed. Data points were found to be scattered near the low hardness region.

Conclusions

The objective of this study was to evaluate the best ways of using waste catalysts as materials in producing pavement tiles. Tile samples were prepared containing various percentages of the waste catalysts and their characteristics were evaluated. Experimental evaluations conducted included: weight loss on ignition; water absorption; porosity ratio; mineralogy determined by XRD; chemical composition by XRF; toxic characteristics by TCLP; leaching concentrations; and particle size distribution.

The following conclusions can be drawn from this study:



(a) 0% **(b) 10%** **(c) 20%**

(d) 30% **(e) 40%** **(f) 50%**

Fig. 11. SEM Micrograph of the Pavement Tiles.

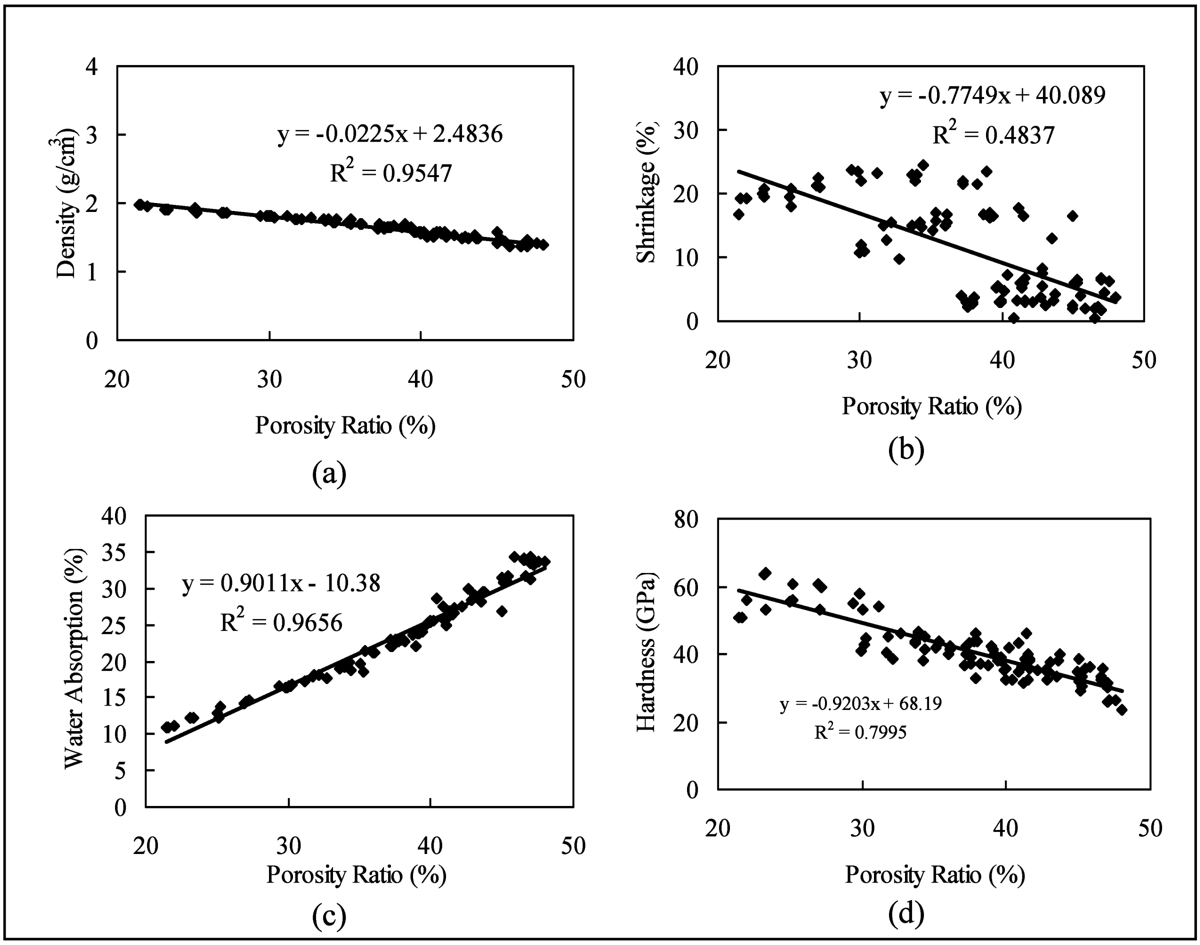


Fig. 12. Relation between the Pavement Tile Properties and Porosity Ratio.

- The water absorption and porosity increased with the amount of waste catalyst used in the mixture.
- Water absorption decreases as the porosity ratio declines.
- The hardness test results of the clay and waste catalyst pavement tiles reveal that the hardness depended strongly on the amount of waste catalyst used as well as the heating temperature.

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