POSSIBLE REUSING OF HOUSEHOLD CERAMIC WASTES AS MINERAL ADMIXTURES IN ECOLOGICAL CEMENT/CONCRETE

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Abstract: Both the Ceramic wastes and the pollution of the cement industry can cause strong damage to the environment and the sustainable development. In the present study, the pozzolanic activity of household ceramic waste powder was investigated by SAI test and Frattini Test; the possibility of the partial substitution of Portland cement blended with ceramic waste powder was analyzed. The results indicate that the compressive strengths of mortar containing ceramic waste at both early age and after 28 days were generally increased as the ceramic waste ratio increased up to at least 15% replacement, and the ground ceramic waste show clear pozzolanic activity.

1 INTRODUCTION

Since 2002, the output of the cement industry in China has been larger than any other country in the world. It is known that around 1 ton of carbon dioxide is emitted for each ton of cement production (Fig.1 (a)). The total cement output was about 2.48 billion tons in 2014, and this trend will continue due to economic growth. Consequently, it is important to take effective measures to reduce the carbon dioxide pollution caused by the cement industry.

Fig.1. Pollution of cement industry and ceramic waste on the environment
(a. Cement industry in China; b. Household ceramic waste)

At the meantime, China is the world's leading manufacturer of ceramics; as a result, more than 100 million tons of ceramic wastes are produced each year in China. The ceramic waste is a serious problem, as there is between 10% and 20% waste from the processing procedures. Only in Guangdong province in south China near Hong Kong, the ceramic waste and waste sludge are about 10 million tons each year. The disposal of this waste not only occupies large areas of land, but can also severely pollute the environment (Fig.1 (b)). Hence, correct treatment of ceramic waste is necessary to preserve the environmental degradation. The reuse of such waste cannot only protect the environment, but also offers a great advantage in partial replacement of cement in concrete for example. As mentioned, more than 2 billion tons of cement is produced annually in China, so 5% replacement of cement would require some 10 million tons of pozzolanic materials and reduce the similar amount of CO_2 emission. That may show significant advantage to both the environment and the sustainable development of the construction industry.

There have been several previous studies that have investigated the use of powdered igneous or metamorphic rocks, as pozzolanic material [1-3] and the use of ceramic waste as aggregate in concrete [4-5]. The investigation on the ceramic roof tile wastes and clay bricks as pozzolanic admixture has been also been conducted [6-7].

In this paper, our attention is focused on the household ceramic (TC) waste from China. In reviewing the literature, few data was found on this topic. The aim of this study is to evaluate the possibility of partial substitution of Portland cement with household waste to produce environmental friendly cement or concrete.

The powdered ceramic waste was used to replace cement in the ratio of 5%, l5% and 25%. The chemical composition, the flowability and crystal structures, especially the pozzolanic activity of the ceramic waste powder is investigated. The results of the study are highly significant for the sustainable development of construction materials as they indicate that the ceramic waste can be reused in partial substitution of Portland cement, and the market for the recycled new pozzolanic materials could be enormous.

2 EXPERIMENT

The experimental program had the following three main aims:

(a) Investigation of the workability of mortars containing household ceramic wastes in comparison with normal cement mortar and cement mortar with fly ash addition.

(b) XRD analysis of ceramic waste powder and its comparison with normal cement and fly ash.

(c) Evaluation of the pozzolanic activity in terms of the Frattini test and SAI test, compressive strength of samples containing household ceramic wastes is compared with that of normal cement and cement mortar with fly ash addition.

2.1 Materials

The household ceramic wastes were obtained from south China. The mix design is listed in Table 1. Cement CEM I 42.5 (CEM-I) with a specific surface area of 330 m^2/kg, fly ash (FA) with the specific surface area of 516 m^2/kg and household ceramic waste powder with a specific surface area 530 m^2/kg were used. The ceramic wastes replace 5%, 15% and 25% of cement. The sand used conformed to ISO 679: 2009 [8]. The water/binder ratio was 0.5.

Table 1 Mix-design of mortars

	Cement (g)	TC/FA(g)	Water(g)	ISO sand(g)	W/B
CEM-I	450	0	225	1350	0.5
TC/FA5	427.5	22.5	225	1350	0.5
TC/FA15	382.5	67.5	225	1350	0.5
TC/FA25	337.5	112.5	225	1350	0.5

2.2 Grain size analysis

Ceramic wastes were ground by a ball mill for 24 hours. The particle size distribution of cement, fly ash and ceramic waste powder (measured by laser granulometry) is illustrated in Fig. 2. It can be seen that for any particular size the percentage of ceramic waste powder and fly ash was greater than that of cement. The most part (almost 100%) of the ceramic waste powder and fly ash was smaller than 40 μm.

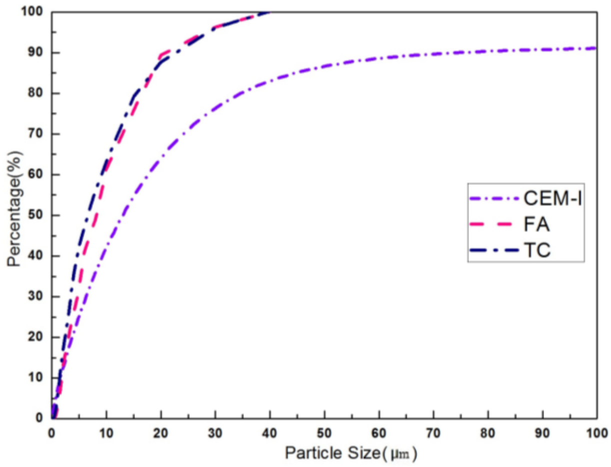

Fig.2. Particle size distribution of materials used

2.3 Chemical analysis

The alkali environment of mortar or concrete matrix is an important factor that affects the durability. The aim of the present investigation was to use the recycled ceramic powder as a part of the mortar or concrete. Hence, the matrix should have a similar alkali ambient to normal cement. The lower boundary of pH value of ceramic waste powder was limited, in order to avoid the reduction of the general alkali value of the concrete matrix. The evaluation of the pH-value of cement, ceramic waste powder and fly ash solution was carried out (see Table 2). It can be seen that pH-value of ceramic waste powder solution is about 10.4 and could be suitable for using in cement or concrete matrix.

Table 2 Comparison of the pH-values

	CEM	TC	FA
pH value	12.46	10.41	11.94

The chemical compositions of CEM, FA and TC were analyzed using X-ray fluorescence and results are presented in Table 3.

Table 3 Comparison of the chemical composition of CEM, FA and TC

	CEM-I(%)	TC(%)	FA(%)
CaO	66.9	0.57	8.25
SiO_2	16.8	71.03	49.1
Al_2O_3	4.36	18.22	26.2
Fe_2O_3	4.19	2.59	10
SO_3	3.89	-	0.533
MgO	1.77	0.33	1.23
K_2O	1.12	4.66	1.58
TiO_2	0.311	-	1.88
Na_2O	0.263	1.03	0.641
SrO	0.253	-	0.198
ZrO_2	0.0646	0.28	0.1
ZnO	0.0429	0.2	0.0361
Cl	0.0339	-	-
PbO	-	0.58	-
CdO	-	0.18	-
Rb_2O	-	0.11	-
BaO	-		0.157
Sum	99.9984	99.78	99.9051

The main chemical components of ceramic waste powder are similar to those of FA and consist mainly of SiO_2 and Al_2O_3, and they are expected to contribute to the pozzolanic activity of ceramic waste powder. The high content of potassium oxide (K_2O) may have a negative effect and the compressive strength of the samples may be reduced.

2.4 Workability of different mixtures

Table 4 illustrates the flowability of mortars with different ratios of ceramic waste powder and fly ash substitutions.

Table 4 Flowability of different fresh mortars

Mixture	CEM-I	TC5	TC15	TC25	FA5	FA15	FA25
Flowability(mm)	176.5	175	189	188	177	184	189

From Table 4, it can be seen that the ceramic waste powder does not exert negative influence on the workability of the mortar if the substitution ratio is lower than 25%.

2.5 XRD analysis

The X-ray diffraction (XRD) testing of cement, fly ash and ceramic waste is carried out to evaluate and compare the crystal structures and amorphous behavior of the materials. The results are presented in Figs. 3.

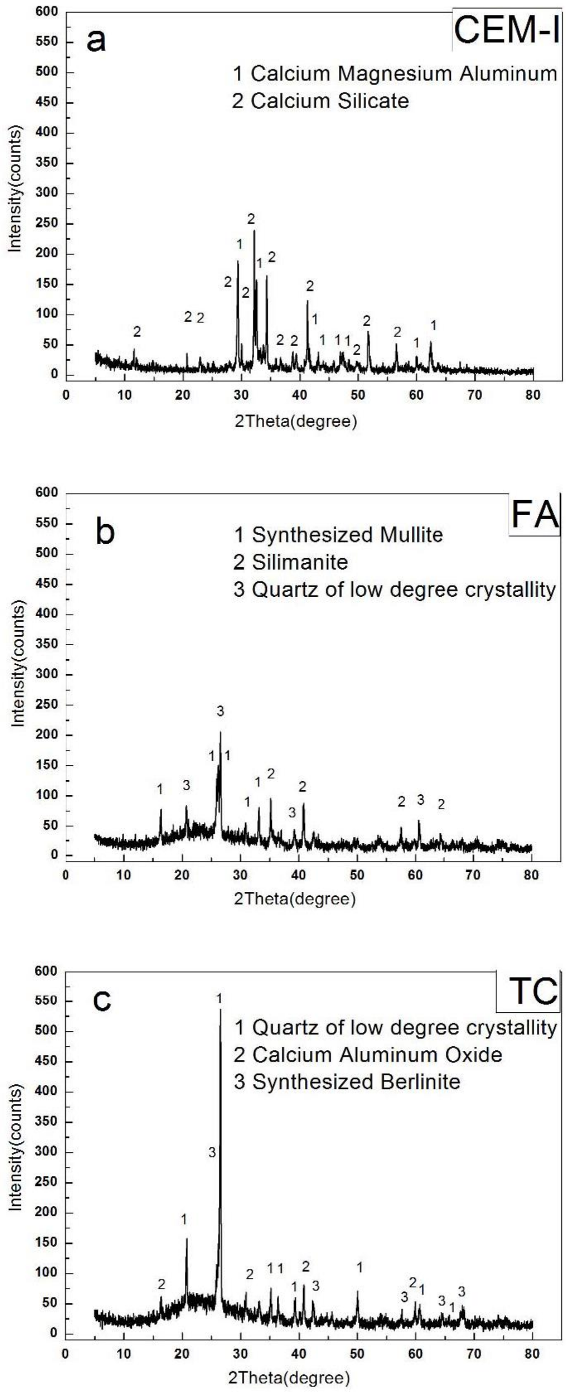

Fig.3. XRD of different powders (a. CEM; b. FA; c. TC)

CEM in Fig.3a shows very slight crystalline behavior. The peak intensity is about 250 counts. The calcium magnesium aluminum is the main crystalline forms detected while calcium silicate is the minor compound. Fig.3b shows that quartz of low degree crystallinity is the main compound with synthesized mullite and silimanite as minor compounds in the fly ash. Fig.3c reflects that quartz of low degree crystal is the main compound detected in the test accompanied with calcium aluminum oxide and synthesized berlinite as the minor compounds in the ceramic waste powder. The low average intensity of TC shows low crystalline degree. Compared to cement and fly ash, it can be seen that ceramic waste powder shows few higher peak intensities due to the slightly crystalline structure (Fig. 3c). It is noted that the average crystalline degree of TC was similar to that of fly ash. The ceramic waste also illustrates clear amorphous structure, which indicates that the crushed household ceramics waste could be used as both pozzolanic material and as fine filler.

2.6 Pozzolanic activity

In order to evaluate the pozzolanic activity, the Frattini test and SAI test were conducted [9-13]. Studies indicate that the Frattini test (direct) and the strength activity index (indirect) are found to be the most accurate and reliable methods to assess pozzolanic reaction of calcined clays to be used in blended cements[11-12], when two direct tests (Frattini and saturated lime) and two indirect tests (strength activity index and electrical conductivity) were evaluated.

In addition, Malquori[13] has suggested that an evaluation of pozzolanic materials for purpose of their addition to Portland cement must be based on two factors: (1) the mechanical strength of mortars and concretes made with a Portland pozzolan mixture, and (2) the reduction of free calcium hydroxide in the hardened pozzolanic cement.

Therefore, in this research work the Frattini test and the SAI test were used to evaluate the pozzolanic activity of ceramics blended cement.

2.6.1 Strength activity index (SAI) of different mortars

The most important quality for pozzolanic activity is seen in the compressive strength. In order to evaluate the compressive strength of blended cement, the concept of Strength Activity Index (SAI) is used. SAI is defined as the ratio of the compressive strength of cement with additional waste powder to the compressive strength of cement without any addition [14–17]. The ceramic waste powder may show pozzolanic activity, if SAI is greater than 0.65[14], 0.8[16] or 0.75[17] with cement replacement of 30%, 20% and 30 after 28 days.

Prismatic specimens of 40 mm x 40 mm x 160 mm were cast and wet cured at 20℃ [14-15]. Results of compressive strengths and SAI values of various mortars at different ages are listed in Tables 5 and 6.

Table 5 Comparison of compressive strengths of various mortars at different ages

	CEM-I	TC5	TC15	TC25	FA5	FA15	FA25
1d	8.95	6.31	9.92	10.64	12.10	9.73	8.50
7d	37.82	36.07	32.79	30.66	36.99	32.64	28.13
28d	45.57	46.52	49.57	44.06	49.55	45.57	38.18

Table 6 Comparison of SAI values of various mortars at different ages

	CEM-I	TC5	TC15	TC25	FA5	FA15	FA25
1d	1	0.71	1.11	1.19	1.35	1.09	0.95
7d	1	0.95	0.87	0.81	0.98	0.86	0.74
28d	1	1.02	1.09	0.97	1.09	1	0.84

In comparison with the CEM samples without waste powder, it can be seen that:

The compressive strength of the samples with 15%and 25% of ceramic waste powder increased 11% and 19% after 1 day, respectively.

After 28 days, the compressive strength of the samples with the mix ratio of 5% and 15% of ceramic waste powder increased slightly, whereas TC25 decreased slightly (3.3%). This implies that 15% of TC could be a possible upper bound for an effective substitution.

- The compressive strength of the samples decreased with the increasing of waste powder and fly ash after 7 days.
- All the SAI values of TC5, TCl5 and TC25 samples without heat treatment are higher than 0.8 and the values of FA, indicating that ceramic waste powders show good pozzolanic activity, which could be very cost-efficient for industrial use.

2.6.2 Frattini Test

The Frattini test was conducted after 8 days curing at 40°C according to the EN 196-5 2011[18]. Results are presented as a hyperbolic curve related to the calcium ion [CaO] concentration versus hydroxyl ion [OH^-] concentration (Fig.4).

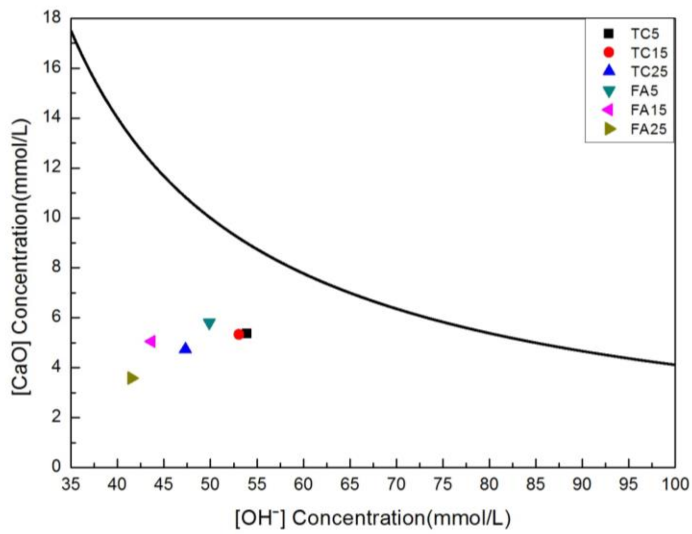

Fig.4. Frattinitest results for blended cement containing TC and FA powder

The interaction relationship of [CaO] and [OH^-] concentrations expresses the lime solubility curve and divides the [CaO] - [OH^-] domain into an upper pozzolanic inactive region and a lower pozzolanic active region. The theoretical maximum [CaO] [19] concentration can be calculated according to Eqn. (1)

$$Max\ [CaO] = 350/([OH^-] - 15) \tag{1}$$

The [OH^-] of various mortars can be compared with the Max [CaO] and the results quantified as the difference between the two values, and they are expressed as the reduction of the Max [CaO]% illustrated in Table 7.

Table 7 Difference of standard calcium hydroxide concentration to the measured concentration

Number	[OH] mmol/L	[CaO] mmol/L	Theoretical max[CaO] mmol/L	[CaO] reduction %
TC5	53.93	5.37	8.99	40.3
TC15	53.07	5.33	9.19	42
TC25	47.29	4.74	10.84	56.27
FA5	49.86	5.81	10.04	42.13
FA15	43.66	5.06	12.21	58.64
FA25	41.52	3.59	13.2	72.8

2.6.3 Comparison of SAI test and Frattini Test

For evaluation of the pozzolanic activity of the waste material, it is important to consider the experimental method used. The Frattini test and the SAI were found to be the most accurate and reliable methods to assess pozzolanic reaction of various materials in blended cements.

The correlation between measured pozzolanic activity of six test materials using the Frattini test and the strength activity index test is illustrated in Fig. 5.

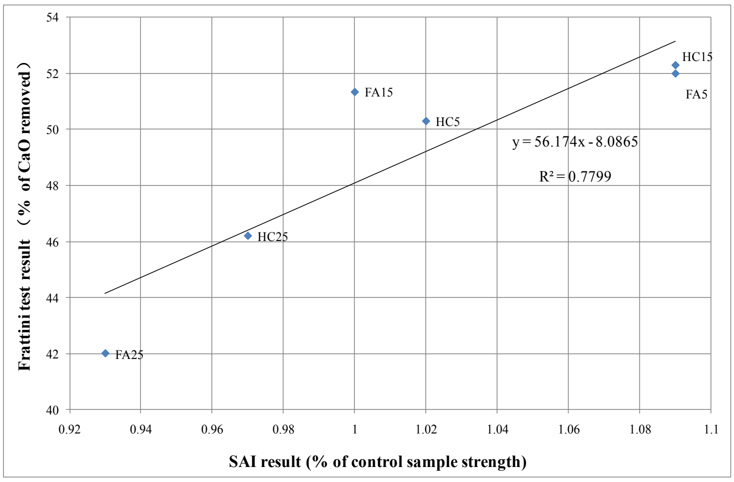

Fig.5. Correlation between pozzolanic activity of FA and HC

It can be seen that there is a significant correlation ($R^2 = 0.78$) between the Frattini test results and the SAI results.

3 CONCLUSIONS

.Mortars with Portland cement, fly ash blended cement, the household ceramic waste powder with cement substitution ratios of 5%, 15% and 25% were experimentally investigated. The pozzolanic activity is an important precondition for recycling of the ceramic waste. The present investigation of ceramic waste powder led to the following conclusions:

- The ceramic waste powder did not have a negative influence on the workability of the mortar for substitution ratio of cement up to 25%.
- Low degree crystalline quartz is the main compound of household ceramic waste

powder, and the ceramic waste shows amorphous structure.

- The compressive strength of TC 5 and TC 15 were higher than those of TC 25 after 7 and 28 days. This implies that 15% of TC could be a possible upper bound for an effective substitution ratio of cement.
- All the SAI values ofTC5, TCl5 and TC25 samples without heat treatment were higher than 0.8 after 7 days.
- The results of Frattini test can be quantified where [OH^-] is in the range 40-55 mmol/l.
- The ceramic waste powder shows high pozzolanic reactivity from 1 day to 28 days by Frattini test and SAI test. There is significant correlation between the Frattini and SAI test results (R^2 = 0.84).

The crushed household ceramic waste powder could be used in cement as both pozzolanic active material and as fine filler. The substitution ratio of 15% of TC appears to be both a reactive efficient point and a possible economically favourable point

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