

Potential Use of Calcined Kaolinite-Based Wastes as Cement Replacements in Concrete – An Overview

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Abstract. The use of supplementary cementitious material (SCM) to partially replace cement is a promising strategy to reduce CO₂ emission and improve the overall sustainability of construction industry. Recent studies revealed that calcined clay could be used as a pozzolanic material and demonstrated an improvement in durability properties of concrete. The pozzolanic reactivity of calcined clay mainly depends on the kaolinite content due to its disordered crystal structure. They can use to replace cement at considerably high level (~30%), and even higher (~50%) if addition limestone powder is used. Since kaolinite is the key source of pozzolanic activity, reusing kaolinite-based waste materials could be a promising and sustainable approach instead of exploiting natural clay for calcined clay cement. This paper summarises recent published works on the use of calcined kaolinite waste as partial cement substitutions in concrete, including thermally activated coal gangue and pre-calcined clay brick and ceramic wastes which have been burnt in their fabrication process. The properties of concrete using these kaolinite-based waste materials are also discussed.

1. Introduction

Ordinary Portland cement (OPC) is the most widely used man-made material in history. The world's cement production was about 4.6 billion tons in 2015 and is increasing by 2.5% annually [1]. Essentially, cement is manufactured by burning limestone and clay at temperature of about 1450°C and generating approximately 0.83 kg of carbon dioxide (CO₂) for 1 kg of cement produced [2]. The cement industry is now considered as one of the highest CO₂ emitting industries contributes to about 7%~8% of global anthropogenic CO₂ emissions [1, 3]. Among the solutions proposed to reduce CO₂ emission in concrete industry, replacing partial cement with supplementary cementitious material (SCM) is one of the most promising strategies. However, in many countries the supply of SCMs is limited. It has been revealed that low-grade kaolinite clay (after heating at 550°C~800°C and grinding into very fine powder) could be used as a pozzolanic material [4]. The pozzolanic reactivity of calcined clay is mainly associated to the dehydroxylation of kaolinite, each of whose layer is built from one tetrahedral silicate sheet and one octahedral aluminate sheet [5]. A study [4] demonstrated that ~30% calcined clay could be used to replace cement and even higher replacement ratio (~50%) of cement can be achieved with the addition of limestone powder.

Besides the exploitation of natural clay, most recent studies [6-19] demonstrated that it is possible to obtain artificial pozzolan from waste kaolinite materials including coal gangue, ceramic waste and fired clay brick. Coal gangue is an industrial solid waste discharged when coal is excavated and washed during the mining procedure. The average generation of coal gangue is about 15% of coal production. In China, it was estimated that about 4.5 billion tons of coal mining waste were stocked and occupied



15,000-hectare lands for the past 9 years, and the rate is increasing by 0.2 billion tons ever year [13, 20]. Ceramic waste is generated during polishing process for a better aesthetics purpose, which refuses about 1%~2% of ceramic products [12]. Each year, 8 million tons of ceramic waste is generated in China and barely recycled [21]. Another potential kaolinite waste is the used old fired clay brick. During the 1980s, most of the residential and low-rise buildings in China were constructed with un-reinforced masonry brick materials. The demolition of these 80s buildings for new city development generates an enormous amount of brick waste (0.4 billion t/y) [22]. Considering the environmental pollution and the consumption of natural lime for cement production, it is crucial to recycle and reuse these kaolinite-containing wastes as an alternative mean to cement.

2. Properties requirements for a calcined kaolinite clay uses as pozzolan

The basic physical and chemical requirements for calcined clay (class N) is shown in table 1. As stated in the table, the percentage of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ should exceed 70 wt%, and the minimum strength activity index for a pozzolanic material at 7 and 28 days should be at 75% or above regardless the substitution rate and curing time [23]. Avet et al. [24] reported that the 28-day compressive strength of mortar utilizing calcined clay correlated linearly to the kaolinite content, and the strength was comparable to OPC mortar when kaolinite content exceeded 40 wt%. Based on this observation, Díaz et al. [25] proposed a preliminary assessment method to use kaolinitic clay deposits as SCM, indicating the desired chemical properties of calcined clay, as shown in table 1.

Table 1. Basic properties requirements for a calcined clay to regard as pozzolan

Chemical and physical properties	Requirement	
	ASTM C 618 [23]	Díaz et al. [25]
$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ (%)	>70	-
Al_2O_3 (%)	-	>18
$\text{SiO}_2 / \text{Al}_2\text{O}_3$	-	>0.3
Loss on ignition (%)	<10	>7
SO_3 (%)	<4	<3
CaO (%)	-	<3
Moisture content (%)	<3	-
Water requirement (% of control)	<115	-
Fineness: amount retained when wet-sieved on 45 μm (No. 325) sieve (%)	<34	-
Strength activity index: with Portland cement, at 7 and 28 days (% of control)	>75	-
Autoclave expansion of contraction (%)	<0.8%	-

3. Coal gangue

3.1. Chemical and mineralogical compositions

The chemical compositions of coal gangues sourced from 16 different locations in China, Spain and USA are displayed in Table 2. The main oxides of coal gangue are SiO_2 (39~60%), Al_2O_3 (15~36%) and Fe_2O_3 (5~20%) satisfy the minimum reactive oxide requirements of ASTM C 618 [23]. The remaining oxides are found to be not significant (below 4%), except a relatively high content of CaO is observed in gangues from Leon [26] and Jiangsu [27]. Loss of ignition (LOI) is relatively high in all investigated coal gangues. The total organic carbon (TOC) of about 15.08 wt% was noticed associated with its LOI value [26]. As for the mineralogical composition, the presence of kaolinite in coal gangue has been reported in many studies by means of XRD [13, 26, 28-30]. According to the quantitative XRD analysis, the major compounds of gangue are kaolinite (20~27 wt%) and illite (45~69 wt%), while the presence of quartz is relatively low (7~16 wt%) [26].

Table 2. Chemical compositions of raw coal gangues (wt%)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Sum*	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	SO ₃	LOI
Leon, Spain [26] ^{1#}	43.70	21.35	5.57	70.62	0.89	0.77	0.16	0.11	1.05	1.02	25.18
Leon, Spain [26] ^{2#}	46.83	17.15	7.67	71.65	7.60	0.99	2.40	0.15	0.78	0.34	15.80
Virginia, US [28]	47.23	14.61	11.94	73.78	4.55	1.68	-	-	-	0.53	11.50
Guizhou, China [10] ^{1#}	45.25	23.34	11.13	79.72	1.88	1.98	0.59	0.58	-	5.67	-
Guizhou, China [10] ^{2#}	46.33	22.68	10.22	79.23	1.56	2.16	0.43	0.66	-	5.35	-
Guizhou, China [10] ^{3#}	38.93	15.33	15.21	69.47	1.03	3.43	0.24	0.46	-	4.98	-
Guizhou, China [10] ^{4#}	42.78	20.88	14.34	78.00	1.92	2.91	0.55	0.57	-	4.33	-
Guizhou, China [10] ^{5#}	49.45	18.92	20.55	88.92	2.05	1.27	0.61	0.72	-	5.01	-
Beijing, China [13]	56.11	16.78	7.02	79.91	3.11	1.68	6.98	1.84	-	-	6.38
Beijing, China [31]	49.41	21.32	6.02	76.75	2.52	1.56	2.85	1.44	0.94	0.65	12.75
Beijing, China [14]	49.90	24.41	6.42	80.73	0.82	1.59	2.06	1.46	0.88	0.12	11.76
Shandong, China [14]	48.82	19.03	4.47	72.32	2.03	2.29	0.19	1.43	-	-	16.78
Shandong, China [7-9]	58.00	17.66	5.23	80.89	1.44	1.60	1.43	0.19	-	2.70	11.52
Jiangsu, China [27]	56.73	23.33	8.45	88.51	9.46	0.12	0.34	0.43	1.13	-	-
Shanxi, China [29]	60.38	24.73	5.76	90.87	0.81	1.37	4.31	0.89	1.36	0.11	-
Shanxi, China [30]	56.56	36.78	1.95	95.29	0.62	0.22	-	0.42	2.10	-	-

*: The Sum of SiO₂, Al₂O₃ and Fe₂O₃.

#: Different coal gangues extracted from the same province/state in the same literature

3.2. Activation treatments

Similar to clay, fresh coal gangue presents no reactivity. Therefore, thermal and physical treatments are essentially needed to activate its pozzolanic reactivity. Studies agree that an optimal temperature should be achieved to maximize the dihydroxylation of kaolinite and prevent its recrystallization. The common activation temperatures used for coal gangue is at 600~700 °C for 2 h in furnace [8, 14, 16, 26, 30]. Calcined coal gangues with a fineness value less than 45~63 μm [16, 26] or about 300~400 m²/kg [7, 13, 14, 30] exhibits good pozzolanic reactivity. Moreover, Li et al. [14] indicated that the effect of fineness on the pozzolanic reactivity of calcined coal gangue is indistinctive when the material is milled to a certain fineness (300~400 m²/kg). Guo et al. [7] suggested that increase the fineness of calcined coal gangue (350~860 m²/kg) can accelerate the early hydration of cement while not significantly effect on the total hydration products. Also, Li et al. [13] used wet milled and calcined the coal gangue with an 8% addition of CaO exhibited better cementitious activity, mainly due to the partial decomposition of feldspar, muscovite and the decreased crystallinity of quartz. Similarly, Zhang et al. [31] and Yao et al. [28] suggested that the combined use of coal gangue and alkaline red mud as cement replacement is favourable, the substitution level of coal gangue and red mud could be up to 50%.

3.3. Effects of calcined coal gangue as pozzolan

Commonly, the pozzolanic reactivity could be evaluated by chemical and mechanical tests. The saturated lime test is a typical chemical test which immerses the calcined coal gangue into saturated lime and takes into account the consumption level of Ca(OH)₂. Frías et al. [16] demonstrated that the fixed lime value of calcined coal gangue is considerable at 1 day, 7 days and 28 days (see in figure 1). As indicated, calcined coal gangue exhibited better pozzolanic activity than metakaolin and fly ash and slightly lower than silica fume especially at the later ages. Moreover, Frías et al. [16] demonstrated use of 10% and 20% of calcined coal gangue as cement replacement had very little effect on the compressive strength of mortar samples. For instance, the reduction of strength at 28 days is only within 4% of mortars containing 20% of calcined coal gangue.

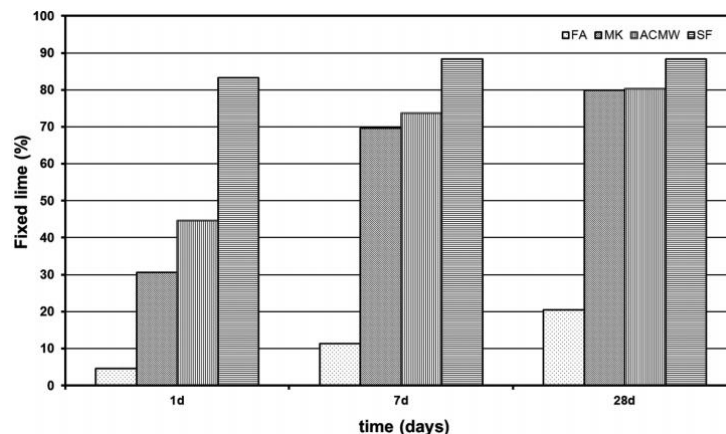


Figure 1. Fixed lime results of fly ash (FA), metakaolin (MK), activated coal mining waste (ACMW) and silica fume (SF) [16]

As for the fresh properties, since the calcined coal gangue used was finer than cement, the mixture required more water to achieve equal consistency [16], with 1.3% and 4.6% extra water was needed for 10% and 20% replacement calcined coal gangue. Moreover, Yi et al. [30] reported that the Al_2O_3 obtained from the dehydroxylation of kaolinite has a strong pozzolanic activity which could bind the chloride ions to form hydrated calcium aluminate. The suggested optimum content of coal gangue is about 20%~30% in order to increase the resistance of cement to chloride attack.

4. Ceramic and clay brick wastes

4.1. Chemical and mineralogical compositions

Ceramic products and clay bricks are manufactured through a combustion process. Detailed procedures and the kiln temperatures used for ceramic and brick production are varying, depend on the clay resources and end-product types. Generally, the kiln temperature for the production of brick is about 800°C~1000 °C [32, 33], while the temperature for ceramic tile is a bit higher, about 1000~1200 °C [34].

The chemical compositions of bricks and ceramic wastes sourced from literature are presented in table 3. The main oxide of ceramic and bricks wastes are quite similar, which mainly comprises SiO_2 (55%~72%) and Al_2O_3 (15% ~20%). In addition, these materials satisfy the requirement of ASTM C 618 [23] for calcined clay as pozzolan materials. As for mineralogical compositions, the existence of amorphous clay phases in ceramic waste was detected ranged from 18°~36° based on the XRD analysis [19]. In contrast, Rojas et al. [35] noticed that the ceramic waste still contains kaolinite which indicated that the pre-calcination during the ceramic manufacture was not sufficient to fully activate the material. As for clay brick, the existence of amorphous structures was observed in the range of 20° to 30° (2θ) under the examination of XRD [17]. Gonçalves et al. [6] estimated that the amorphous content of brick waste was about 61%. As compared to commercial metakaolin, the amorphous content is about 87%.

Table 3. Chemical compositions of ceramic and clay brick wastes (wt%)

	SiO_2	Al_2O_3	Fe_2O_3	Sum*	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	SO ₃	LOI
Ceramic waste [19] ^{1#}	66.40	21.00	1.70	89.10	1.80	1.20	2.50	3.30	0.77	-	0.5
Ceramic waste [19] ^{2#}	66.00	20.90	1.70	88.60	3.10	1.10	2.30	2.60	0.76	-	0.50
Ceramic waste [35]	61.80	15.10	0.79	77.69	3.50	10.00	2.40	1.80	-	0.10	3.63
Ceramic waste [11]	65.90	17.30	1.00	84.20	2.10	4.70	1.90	1.80	0.20	-	3.80
Brick waste [17]	66.52	14.20	5.45	86.17	6.06	2.35	2.09	0.67	-	0.75	-
Brick waste [36]	62.70	17.10	6.84	86.64	3.94	2.25	1.23	1.39	-	0.84	2.67
Brick waste [6]	63.89	25.49	7.73	97.11	0.29	0.04	0.95	-	-	-	-
Brick waste [18]	65.89	23.28	6.15	95.32	-	-	1.35	1.85	-	-	0.85
Brick waste [15] ^{1#}	54.83	19.05	6.00	79.88	9.39	1.77	3.15	0.50	-	-	-

Brick waste [15] ^{2#}	69.99	10.62	4.02	84.63	8.86	1.39	2.61	1.02	-	-	-
Brick waste [15] ^{3#}	68.79	15.23	6.28	90.30	1.79	2.02	3.71	0.26	-	-	-
Brick waste [15] ^{4#}	72.75	15.89	4.97	93.61	0.87	1.20	2.17	0.27	-	-	-

*: The Sum of SiO₂, Al₂O₃ and Fe₂O₃.

#: Different wastes utilized in the same literature

4.2. Effect of ceramic waste as pozzolan

Rojas et al. [35] carried out a saturated lime test to examine the pozzolanic activity of ceramic waste. The results indicated that the pozzolanic activity was not high in the early age, while it became comparable to fly ash at 28 days and close to silica fume at 90 days.

Steiner et al. [19] compared the compressive strength results of mortar incorporating 0~40% ceramic waste at different ages (Figure 2(a)). It showed that due to the increased amount of ceramic wastes the compressive strength decrease regardless of its curing time. The strength developments of mortar samples before 28 days were not obvious, reflecting weak pozzolanic effect in the system at early ages. Rojas et al. [35] also indicated that with the incorporation of 20% ceramic waste reduced the 28 days compressive and flexural strength by 10%. Besides, it has been demonstrated that the use of ceramic waste increased the onset time shrinkage of mortar and decreased the total autogenous shrinkage [19] (Figure 2(b)).

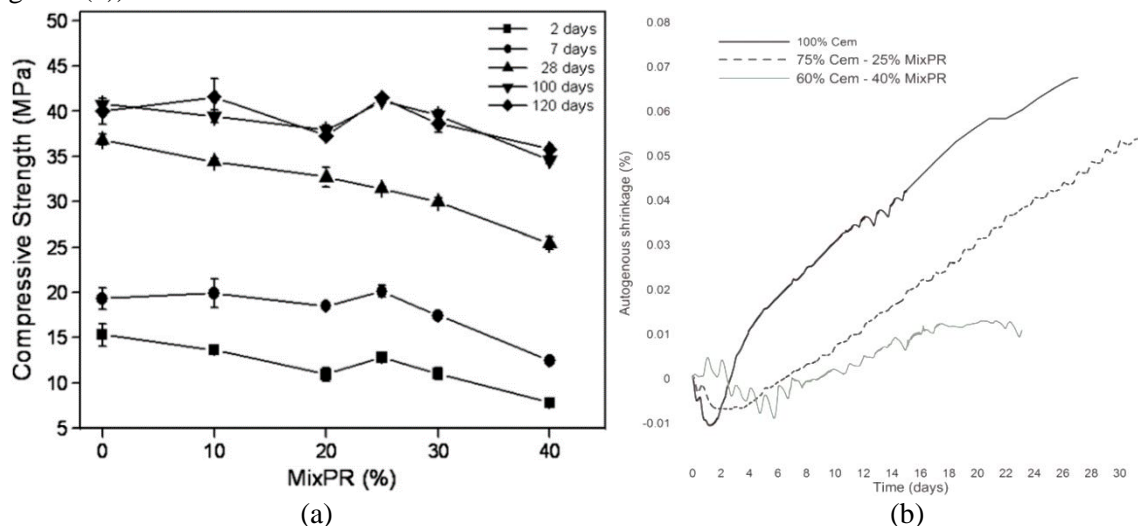


Figure 2 Compressive strength (a) and autogenous shrinkage (b) of mortar with ceramic waste [19]

4.3. Effect of clay brick waste as pozzolan

Naceri and Hamina [17] indicated that the increase of the brick waste resulted in a reduction of compressive and flexural strength of mortar at 7 and 28 days. At 90 days, mortars with up to 10% of brick waste remained a comparable mechanical strength. But significant reductions of strength were reported with higher replacement level. Similar finding was also reported by Gonçalves et al. [6], where the effect of 20% brick waste in mortar has less impact on compressive strength, but a further increment of brick waste resulted in a significant reduction of compressive strength. Apart from mechanical strength, the use of brick waste could also reduce the elastic modulus [6] and shrinkage issue of a cement mortar [17].

5. Conclusion

This paper discussed the potential and effect of using thermally activated coal gangue and pre-calcined ceramic and clay brick wastes as pozzolan in cement-based materials. Based on the results published in the literature, the following findings can be drawn:

- Calcined coal gangue, ceramic and clay brick wastes can be used as artificial pozzolans with proper pre-treatments.
- An optimal thermal treatment (600°C~700 °C) and physical grinding (fineness of 300~400 m²/kg) can effectively activate the reactivity of coal gangue.
- Generally, the use of these kaolinite-based wastes reduces the initial and final setting time of mortar, and they also slightly affect mortar mechanical strength when replacement is low. Possible replacement limit for these wastes to be used in mortar is 20%
- The heating process of ceramic products and clay brick has obviously affect the reactivity when they are recycled and grinded for use as pozzolan in cement-based materials.

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