

STUDIES ON REACTIVITY OF LIMESTONE-CALCINED CLAY CEMENT FOR SUSTAINABLE INFRASTRUCTURES

Geetika Mishra*, Anuj Parashar, Shashank Bishnoi

Indian Institute of Technology Delhi, INDIA *E-Mail: geetika.mishra30@gmail.com

Abstract: In the present scenario, urbanisation is accelerating at an exponential rate all around the world and approximately 70% population is expected to be living in urban areas by 2030. This rapid urbanization has created a challenge before construction sector to develop sustainable and durable building materials with minimal emission of Green House Gases (CO2) during their production without compromising their performance. In this regard, reducing the cement clinker content might have positive effects on the environmental aspects of concrete, where Limestone calcined clay cement (LC3) is found to be more promising than other blended cements. In the present study, different combinations of clays and limestones were used to prepare blends. The existing testing techniques for the pozzoloan potential are still same. This raise a question of applicability of existing techniques of reactivity potentials of supplementary cementitious materials (SCMs) over their blends. This study will look for the similarity in phase formed during the hydration of blends in Ordinary Portland cement (OPC) as well as Calcium hydroxide (CH) system. Similar products formation can conform the applicability of exiting testing techniques to their blends also. Therefore, the blends of calcined clay and limestone were mixed with pure CH and OPC system to monitor their reactivity. For characterizing the reactivity of blends X-ray diffraction technique was used. The reactivity of blends in two different system (CH and OPC) are being compared to observe the potential of claylimestone blends in cement as well. From the study it has been found that the product form are same in CH and OPC system, which allows exiting technique applicability on blends of SCMs.

Keywords: Calcined clay; Limestone; Cement; Reactivity; Calcium hydroxide;

1. Introduction

Reducing the consumption of cement with simultaneous utilizing SCMs is preferred for reasons of environmental protection. As per standards, typical content of **SCMs** percentage substituting cement in blended cements (Binary or Ternary) does not exceed 35% of mass of binder. Globally, more and more interest is aroused to the increase replacement level of cement with supplements above 50%. This may change the mechanism of hydration processes, which will increase the complexity of the system. Most popularly Fly ash, GGBS, Silica fume, Metakaolin etc are being used replacing materials without as а compromising with the performance of cement and to reduce carbon footprint. Among these SCMs, the production of Metakaolin or calcined clays is pointed out as a possible candidate to overcome problem of CO₂ emission to some extent.

Therefore, efforts are being made in reducing clinker the cement content replacing with Limestone-calcined clay blends. Kaolinite [Al₂Si₂O₅(OH)₄], which is theoretically composed of 46.54% SiO₂, 39.50% Al₂O₃ and 13.96% H₂O, when ignited at higher temperature 500-800°C, it forms metakaolin (Calcined clay) $[Al_2Si_2O_7]$ through the loss of the lattice oxygen and hydroxyl groups [1,2]. It is well known that hydration of Portland cement results in formation of hydrated products such as calcium-silicates-hydrate (C-S-H), calcium hydroxide (CH), hydrated calcium aluminates and sulfoaluminates (AFm, AFt) as well as similar products with iron ions [3].

Combination of cement and SCMs, leads to complicate the systems in which cement hydration and pozzolanic or hydraulic reactions with SCM may occur at the same time. Both cement and introduced additives



may interact on each other and modify their reactivity and nature of hydration products. Kinetics of reaction of such materials in the hydrating cement environment depends on their chemical composition, the amount of reactive phases (e.g. amorphous silica), fineness, pH, temperature etc. [4]. It is assumed that in the presence of silica or aluminosilicate additives the hydration products are similar to those that are formed during the hydration of cement. In C-S-H phase formed fact, the with additive pozzolanic has а lower calcium/silica (Ca/Si) ratio, resulting in increased capture of aluminum ions from a solution, which are incorporated into the structure of the C-S-H. Chemical composition and reactivity of cement replacing material may also influence the amount of ettringite, AFm phases such as monosulfate or monoaluminate as well as strätlingite [4]. For example, in the presence of spent aluminosilicate, CH precipitated in the Portland cement hydration is converted to C-S-H due to pozzolanic reaction. As a result, the cement paste with the addition contains a smaller amount of calcium hydroxide and a greater amount of phases of aluminate hydrates.

The interest of the present study is to look for the applicability of existing test methods for reactivity potential of SCMs to the blends. As most of the methods such as Lime reactivity as per Indian Standard, Chapelle's test as per Europian standard and some calorimetry techniques are purely performed in the presence of CH only. Currently there is no standardised technique which can look for the reactivity of blends. If the product formed during the reaction of CH and SCMs blend are simillar in OPC system also then it shows a possibility of using existing methods for the blends of SCMs. The idea in this case was to enhance the reactivity of metakaolin-cement blends to enable the use of calcined impure, kaolin-containing clays as SCMs. Calcined impure clays have a lower reactivity compared to pure metakaolin [5,6], however they are desirable as SCMs due to higher availability and lower cost compared to

pure kaolinite. Enabling the use of impure clays, by compensating for the lower reactivity may facilitate their use as SCMs.

2. Experiments

2.1 Materials

Ordinary Portland Cement of 43 grade is used to make LC³. Two types of calcined clay (clay I and clay II) and limestone (LS) are mixed in different proportions in making LC³, chemical composition of each materials are given in Table 1. The composition of the mix blended are given in Table 2. Standard sand of three grades (I, II, III) were used for mortar casting.

Table 1 – Chemical composition of raw materials

Composit ions	Clinker	Clay I	Clay II	LS
CaO (%)	65.16	0.54	0.06	44.24
SiO ₂ (%)	21.07	51.16	54.67	11.02
Al ₂ O ₃ (%)	4.65	36.13	27.69	2.53
Fe ₂ O ₃ (%)	4.32	1.15	4.93	1.55
Na ₂ O (%)	0.38	0.10	0.12	0.50
K ₂ O (%)	0.20	0.04	0.26	0.28
LOI (%)	0.96	8.24	10.28	36.96

2.2. Methodology

2.2.1. Sample preparation for Compressive strength

First of all, blends with calcined clay and limestones were prepared in different proportions as presented in Table 1. Thereafter, these blends were thoroughly mixed with cement and gypsum till the homogeneous colour of the mix appeared. For preparation of mortar cubes, cement and sand ratio was taken as 1:3 and waterto-cement ratio kept constant for all mixes at 0.45. As per IS 4031 (part 6) cubes of dimension 7.06×7.06×7.06 cm³ were cast and demoulded after 24hr. Afterwards, these cubes were cured at 27±3°C till the testing age. Three cubes of each were tested and



Blends	Cement	Calcined	Limestone (%)		Gypsum	Quartz*
	(%)	Clay	Calcite	Dolomite	(%)	(%)
Mix 1	50	30.6 (I)	15.3	-	4	-
Mix 2	50	23	23	-	4	-
Mix 3	50	15.3	30.6	-	4	-
Mix 4	50	30.6	-	15.3	4	-
Mix 5	50	30.6 (II)	15.3	-	4	-
Mix 6	50	30.6	-	-	4	15.3

Table 2: Composition of LC³ prepared

*Quartz was used as a filler

their average is reported at 1, 3, 7, 28 day of testing.

2.2.2. Sample preparation for XRD analysis

XRD analysis was carried out on the paste of cement+blends and blends individually. In this method, clay-limestone blends mixed with calcium hydroxide in 1:1 ratio and similarly on the other hand, blends mixed with cement to observe the potential of claylimestone blends in cement as well. At each hydration ages such as (3, 7 and 28days) samples were sliced and to avoid any carbonation immediately used for XRD analysis.

3. Results and Discussion

3.1 Compressive strength

Fig. 1 shows the change in compressive strength of the mix with different blends. Results revealed that Mix 1 (containing clay I+LS1 into 2:1 ratio) showing highest every age of hydration strength at compared to other mixes. This may takes place due to the presence of highly pure clay and limestone. Clay I is highly pure containing about 80% Metakaolinite, which is amorphous in nature and highly reactive towards Ca2+ consumption (present in cementitious system). This mechanism is pozzolanic called reaction, wherein amorphous silica (SiO₂) comes in contact with water to form silicic acid and these silicic acid ions react with the CH to formed calcium-silicate-hydrate (C-S-H). C-S-H gel is the main strength imparting phase among all cement hydration products.

Mix 2 and 3 are also the blends of Clay I and LS1, while the ratio of their mix are different such as 1:1 and 1:2, respectively. Strength with the Mix 2 slightly decreases as compared to Mix 1, it may be due to decrease in percentage of clay I, which was required to consume calcium hydroxide in the system. Thus, less C-S-H is supposed to form. Similarly, in Mix 3, there is further significant reduction in strength took place, suggested that more part of clay was replaced with limestone, which only work as a filler instead of any chemical reaction (pozzolanic reaction). Therefore, the overall strength is lower than Mix 1 and 2.

Additionally, Mix 4 is similar in composition of Mix 1 except limestone, wherein limestone was replaced with dolomitic limestone. It shows lower strength at early ages. Further, Mix 5 (containing clay II+ LS1), which is showing less strength and indicating that this clay is



Fig. 1: Compressive strength of blends with cement

comparatively less reactive as compared to clay I.

3.2 XRD analysis

The XRD profile blends of (Clay+Limestone) mixed with CH and OPC are shown in Figs. 2 and 3. The XRD patterns for the calcined clay+limestone system show the calcium carbonate peak at 29.5° **(2θ)** and reducing quantity of Portlandite at 18.2° (20). In the Mix 1 Cement+ (containing calcined clay+limestone) there are ettringite and strätlingite at 7, 28 days, along with very less Portlandite.



Fig.2: XRD profile of Calcined clay+limestone blend with CH at 3, 7 and 28 day



Fig. 3: XRD profile of Mix 1 at 3, 7 and 28 days of hydration

The reactivity of SCMs can be best measured with the consumption of CH. In this paper similar approach is being followed to find the reactivity of these blends within CH and cement system. For this observation main focus is drawn towards the change in the intensity of CH peak and appearance of any new peak due to development of any new phase. From the Fig. 4, it can be seen that the peak of CH (18.2°) is still appearing in CH+Blends system, while in OPC+blends this peak is totally disappear. This result revealed that with 50% clinker replacement formation of CH is decreased and the amount formed during hydration is already consumed by amorphous silica part of calcined clay, thus the peak of CH completely disappeared at 28 day.



Fig.4: XRD profile of Blends within CH system

In OPC+blends system, all other peaks are same as formed in plain OPC, with the replacement by blends not major changes are observed. At ~10.9° (2 θ), development of carboaluminate peak is observed, it may happen due the presence of limestone with in the blends, where the ratio of limestone is high peak is also significantly higher than other mix. Therefore, form these results it can be observed that the reactivity of the blends only affect the formation of CH, rest of phases are same as formed in Plain cement.



Fig.5: XRD profile of Blends with OPC

4. Conclusions

Reactivity of the SCMs with CH and OPC has

been carried out and from the results it can be concluded that:

- Calcined clay and limestone blend effectively improve the compressive strength of the system due to the pozzolanic reaction of amorphous silica with CH and results into more C-S-H as well as more strength.
- Inspite of presence of various method to determine lime reactivity of SCM, XRD can be a better tool to observed lime consumption capacity of different SCMs.
- Most important, this study show that the product form are same in CH and OPC system, which allows exiting technique applicability on blends of SCMs.

References

- Sakizci M, Alver BE, Yörükog ullari E. Thermal behavior and immersion heats of selected clays from Turkey. J Therm Anal Calorim 2009;98:429–36.
- [2]. Samet B, Mnif T, Chaabouni M. Use of a kaolinite clay as a pozzolanic material for cements: formulation of blended cement. Cem Concr Compos 2007;29:741–9.
- [3]. Kurdowski, W., Chemia cementu i betonu, Wyd. Polski Cement, Wyd. Naukowe PWN, Kraków 2010.
- [4]. Lothenbach, B., Scrivener, K., Hooton, R. D., Supplementary cementitious materials, Cement and Concrete Research 41, 2011, 217-229.
- [5]. Samet B, Mnif T, Chaabouni M., Use of a kaolinite clay as a pozzolanic material for cements: formulation of blended cement. Cement and Concrete Composites 2007;29:741–9.
- [6]. He C, Osbaeck B, Makovicky E. Pozzolanic reactions of six principal clay minerals: activation, reactivity assessments and technological effects. Cement and Concrete Research 1995;25(8):1691–702.