Influence of Calcium Sulphate on Hydration of Cements Containing Calcined Clay

Gopala Rao Dhoopadahalli, Sreejith Krishnan and Shashank Bishnoi

Abstract The present study tries to understand the effect of sulphates on the hydration of Portland cement—calcined clay systems. Calcined clay was obtained by calcining a clay having 95% kaolinite at temperatures ranging from 700 to 800 °C. The calcined clay was used to replace 30% of clinker. A clinker with low aluminate and low alkali content was used. Laboratory grade gypsum was used as the source of sulphates. In this study, the sulphate content in the cement system was varied as 2.5 and 5.0%. Mainly, the effect of sulphates on the hydration of cement was studied by conducting isothermal calorimetry on cement pastes for 48 h. In addition, the phase assemblage studies were done at 1 day and 3 days by performing X-ray diffraction on the paste samples. It was observed from calorimetry that the blends with higher sulphate content show a significant delay in aluminate hydration. It was again noticed that the main hydration peak was also affected with increase in sulphates. In calcined clay blend, the amount of ettringite formed was lesser than the normal OPC blend at similar sulphate content. In the other case where the dosage of sulphate was high, the ettringite continues to form till 3 days.

Keywords Calcined clay · Calcium sulphate · Hydration

1 Introduction

The manufacturing of cement contributes significantly to overall CO_2 emissions at various stages of its production, starting from quarrying to packing. Out of all the processes involved, the CO_2 emitted during limestone decomposition and burning of fuel in the kiln accounts to major portion of overall CO_2 emission, which are

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unavoidable. In order to reduce the overall CO_2 emissions, cement industry is constantly undertaking huge efforts like improving the processes by adopting state of the art technologies, utilisation of alternative fuels, etc. The present trend in cement industry is to achieve lower clinker factors in cements without compromising on performance. Binary and ternary blended cements are prepared by replacing some portion of clinker with one or more supplementary cementitious material (SCM). Calcined clay or metakaolin is one such SCM that can be used for replacing cement.

Metakaolin is obtained from calcining a clay having high amount of kaolinite ($Al_2Si_2O_5[OH]_4$) mineral. These kaolinitic clays are calcined at temperatures ranging from 500 to 850 °C to make it a pozzolanic material [1–4]. The temperature up to which it should be calcined is still a question of debate. It is reported that highest pozzolanic reactivity is achieved by calcining at 800 °C [1]. However, beyond 850 °C, if calcined, clay may transform to less reactive crystalline material like cristobalite and mullite [5]. Furthermore, it must be noted that even the duration to which the clay is subjected to calcination can influence the properties of calcined clay.

Calcined clay rich in amorphous alumina and amorphous silica readily reacts with water and $Ca(OH)_2$ liberating enormous amount of heat. The reactivity of calcined clay depends largely on the type of cement and the same is delayed when used with low C_3A cement [6]. It has been reported that the pozzolanic reaction is more in clays containing lesser amount of kaolinite replaced at higher levels [7]. Calcined clay contains high alumina and is finer than ordinary Portland cement (OPC). Thus, sulphates are added in extra quantities in calcined clay blended cements to control the hydration reaction. In addition to controlling the aluminate hydration, sulphate can also influence other reactions. Hence, it becomes necessary to investigate the influence of sulphate in cements blended with calcined clay. The current study is mainly focused on isothermal calorimetry and phase assemblage studies during initials ages of hydration.

2 Materials and Methods

The oxide composition of clinker and calcined clay used in making the cements is presented in Table 1. Cement with low C_3A and low alkali content was intentionally chosen to better understand the reaction of calcined clay which is rich in aluminates.

Table 1 Chemical composition of clinker and calcined clay

Oxides (%)	CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SO_3	MgO	TiO_2	Cl
Clinker	65.02	19.83	5.06	5.46	0.52	0.00	1.48	1.16	0.71	0.00
Calcined clay	0.17	48.08	46.57	0.82	0.02	0.41	0.17	1.49	1.93	0.18

Precisely, the clinker contains 52.14% C_3S, 29.08% C_2S, 1.41% C_3A and 17.36% C_4AF.

The calcined clay procured from industry was not calcined properly as some amount of kaolinite was still left in it. Consequently, the calcined clay procured was again calcined at 800 °C in a muffle furnace for 1 h. The X-ray diffractograms of both originally procured calcined clay and the treated calcined clay are shown in Fig. 1 and their phase composition is shown in Table 2. The amorphous content has been increased drastically after calcination indicating the complete conversion of kaolinite to metakaolin (Table 2). The treated calcined clay and the clinker are then subjected to particle size analysis. The particle size distribution results are presented in Table 3.

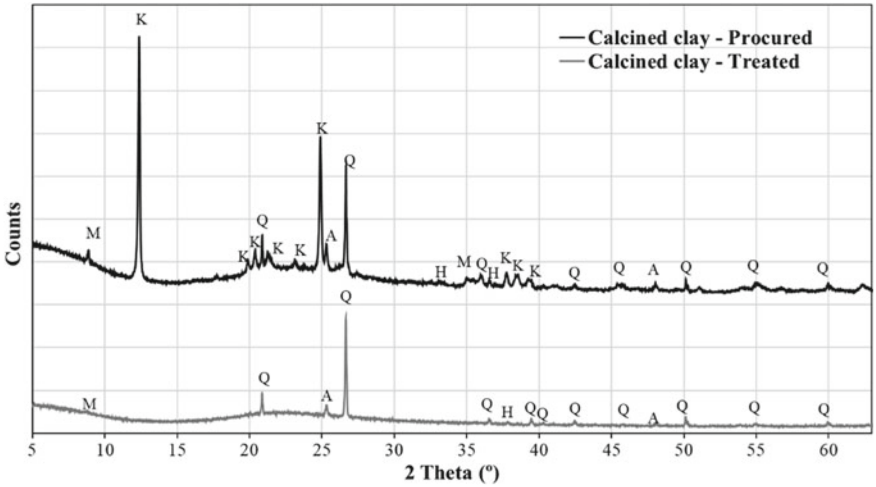

Fig. 1 XRD of calcined clay (K-Kaolinite, Q-Quartz, A-Anatase, M-Muscovite and H-Haematite)

Table 2 Phase composition of calcined clay before and after calcining in muffle furnace

Phase name	Calcined clay—procured	Calcined clay—treated
Kaolinite	15.63	0.16
Quartz	4.04	5.96
Muscovite	1.42	0.60
Hematite	0.80	0.26
Anatase	1.38	0.76
Total amorphous	76.73	92.27

Table 3 Physical properties of clinker and calcined clay

Parameter	Clinker	Calcined clay
Specific gravity	3.2	2.59
D_{10} (µm)	3.43	3.32
D_{50} (µm)	15.2	10.7
D_{90} (µm)	70.8	32.8

Table 4 Material proportions for blend preparation

Blend	Clinker	Calcined clay	Gypsum
OPC-2.5	94.63	–	5.38
CC-2.5	66.24	28.39	5.38
CC-5.0	62.48	26.78	10.75

Calcium sulphate dihydrate obtained from Merck which is of laboratory grade with 99% purity was used in all the blends. The sulphate content in cements was varied as 2.5 and 5.0%. The proportions of various materials required in the preparation of each blend are shown in Table 4. The blend OPC-2.5 was treated as the control blend to which the other blends were compared.

3 Tests Performed on Cement

3.1 Isothermal Calorimetry on Cement Pastes

Isothermal calorimetry test was conducted to know the effect of sulphate addition on heat evolution in cements at early stage. All the materials required for the test were stored in a closed chamber where temperature was maintained as 27 °C always. The pre-conditioning of materials was done for 24 h. A fixed water to cement ratio of 0.40 was used to make the cement paste. After thorough mixing, the paste was transferred to calorimeter cups immediately. The cups were closed properly and placed inside the isothermal calorimeter (Calmetrix I-cal 8000) for logging. And the logging was carried out for 48 h.

3.2 X-Ray Diffraction on Cement Pastes

The cement paste was made as described in Sect. 3.1. The paste was filled in 2 cm diameter cylindrical tubes and allowed to mature till the day of testing. At 1 day and 3 days, the hardened paste was taken out of the tube and 3 mm thick slices were cut with the help of precision saw. The slices made were scanned in X-ray diffractometer (Bruker D8 Advance Eco). The scan was performed from 5° to 65°

(2-theta) with a step size of 0.019° and 0.3 s per step. The scan files were analysed by performing Rietveld refinement by external standard method. High purity rutile was used as an external standard. The hydration products like ettringite and portlandite were quantified at 1 day and 3 days.

4 Results and Discussions

4.1 Hydration Studies

The rate of heat evolution curve for all the blends is shown in Fig. 2. The rate of heat evolution at induction period and at silicate peak and the slope of the curves at acceleration period are calculated and are presented in Table 5. The rate of heat evolved at induction period and at silicate peak is more for CC-2.5 compared to OPC-2.5 (Table 5). On the other hand, the rate of heat evolution at silicate peak is less for CC-5.0 compared to control blend. A clear aluminate peak is not observed in

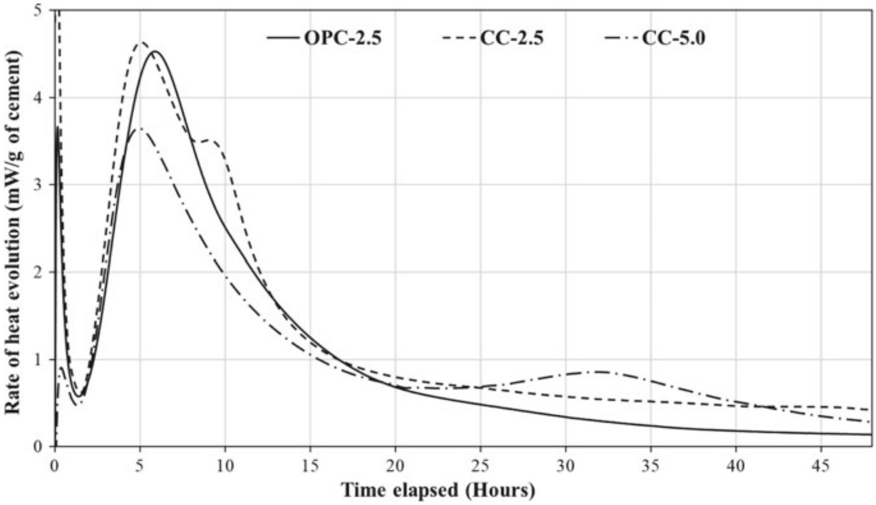

Fig. 2 Rate of heat evolution in blends OPC-2.5, CC-2.5 and CC-5.0

Table 5 Salient features from calorimetric curves

Blend	Rate of heat evolution at induction period (mW/g)	Rate of heat evolution at silicate peak (mW/g)	Slope of the curve during acceleration (mW/g-hour)
OPC-2.5	0.57	4.53	1.21
CC-2.5	0.62	4.63	1.55
CC-5.0	0.47	3.65	1.24

OPC-2.5 as it is a low C_3A cement. However, in CC-2.5 and CC-5.0 the aluminate peaks occur at 9 h and 32 h, respectively.

Among all the blends, the rate of heat evolution is more in CC-2.5 at induction period which indicates early onset of acceleration period. It is also evident from the slope of acceleration curve (Table 5) that the reaction occurs at a faster rate during the acceleration period in CC-2.5 blend indicating the early activity of aluminates. The higher rate of heat evolution in CC-2.5 blend during acceleration period is the combined effect of OPC hydration and pozzolanic reaction. The same is not observed in CC-5.0 blend because it has lower clinker content and due to significant delay in the hydration of aluminates. It is also seen that the reaction of aluminates is delayed significantly at higher dosage of sulphates. The aluminate hydration appears as a shoulder peak in CC-2.5 around 9 h and the same is observed as a broad hump in CC-5.0 with its peak occurring around 32 h (see Fig. 2).

The cumulative heat released curve for all the blends is shown in Fig. 3. It is clearly observed from the curves (see Fig. 3) that at the end of 48 h, calcined clay blends CC-2.5 and CC-5.0 are releasing more heat than the control blend OPC-2.5. At all times, the cumulative heat energy released is more in CC-2.5 compared to the other two blends. At initial stages, till 5 h the heat energy released is same for both OPC-2.5 and CC-5.0 but in OPC-2.5 the heat released increases gradually thereafter. However, after 30 h, the heat energy value increases rapidly because of delayed aluminate hydration in CC-5.0 blend. Also, the energy gap between OPC 2.5 and CC-5.0 goes on reduces. Finally, at 38 h, CC-5.0 curve crosses OPC-2.5 curve around 32 h indicating the delayed activity of aluminates. Overall, after 48 h, both calcined clay blends release more heat than the control one showing that the effect of reduction in clinker is well compensated by the calcined clay.

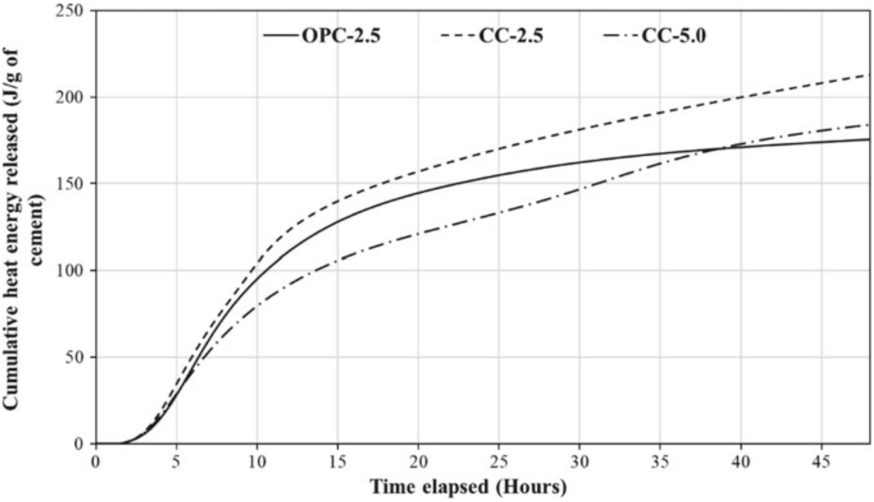

Fig. 3 Cumulative heat energy released in OPC-2.5, CC-2.5 and CC-5.0 blends

Table 6 Ettringite and portlandite formed in g per 100 g cement paste after 1 and 3 days

Blend	Ettringite at 1 day	Ettringite at 3 days	Portlandite at 1 day	Portlandite at 3 days
OPC-2.5	14.16	16.77	7.09	10.08
CC-2.5	10.90	10.10	3.55	4.71
CC-5.0	18.08	21.54	3.85	2.53

4.2 Phase Assemblage Studies

The phase assemblage studies are carried out on hardened cement paste specimens to know the effect of sulphate content on the formation of hydration products. The quantity of ettringite and portlandite formed at the end of 1 day and 3 days is presented in Table 6.

The quantity of portlandite is increased in OPC-2.5 from 1 day to 3 days due to hydration of silicates. Likewise, in CC-2.5 there is an increase in portlandite content from 1 day to 3 days. However, in CC-5.0 blend, a reduction in portlandite content is observed from 1 day to 3 days. It is reported that in properly sulphated cement, in the presence of gypsum, the dissolution of Ca^{2+} ions increase [8]. Also, it has been reported that C_3S hydration is increased when both C_3A and sulphates are present and the same is decreased when aluminium ions are present [9]. In CC-5.0 blend, the portlandite content is more at 1 day compared to CC-2.5 might be due to enhanced silicate reaction at higher sulphate content.

In low C_3A clinker, the reaction of calcined clay is slow [6] and hence there is an increase in portlandite content from 1 day to 3 days in CC-2.5 blend. However, the same trend is not observed in CC-5.0 blend. At higher sulphate dosages, i.e. in CC-5.0 blend, the rate of depletion of $CaOH_2$ is faster than its rate of formation. Thus, a reduction is observed from 1 day to 3 days in portlandite content which may be due to more pozzolanic reaction.

In control blend OPC-2.5 the sulphate to alumina ratio is high and thus the quantity of ettringite is increased from 1 day to 3 days (Table 6). However, a reduction in ettringite content is observed from 1 day to 3 days in CC-2.5 blend. In blend CC-2.5, the reactive alumina content is more, and the sulphate content is same as in OPC-2.5 leading to reduction in sulphate to alumina ratio which favours the AFm transformations. Furthermore, in CC-5.0 where there is ample amount of sulphates, ettringite quantity is increased from 1 day to 3 days. It is reported that the alumina uptake can take place in C-S-H resulting in C-(A)-S-H formation in calcined clay rich in kaolinite content [10]. However, at higher dosage of gypsum, where sulphate to alumina ratio is high ettringite formation is favoured instead of C-(A)-S-H.

5 Conclusions

The following conclusions were drawn based on hydration and phase assemblage studies conducted on calcined clay blends.

- Though, the aluminate peak is significantly delayed in Portland cement—calcined clay systems, overall heat is more than the control OPC blend at 48 h.
- The initial hydration of silicates may be affected due to higher sulphate contents.
- At higher dosage of sulphates, ettringite is formed at the expense of C-(A)-S-H.

References

1. Alujas, A., Fernández, R., Quintana, R., Scrivener, K.L., Martirena, F.: Applied clay science pozzolanic reactivity of low grade kaolinitic clays: influence of calcination temperature and impact of calcination products on OPC hydration. Appl. Clay Sci. **108**, 94–101 (2015). https://doi.org/10.1016/j.clay.2015.01.028
2. Almenares, R.S., Vizcaíno, L.M., Damas, S., Mathieu, A., Alujas, A., Martirena, F.: Case studies in construction materials industrial calcination of kaolinitic clays to make reactive pozzolans. Case Stud. Constr. Mater. **6**, 225–232 (2017). https://doi.org/10.1016/j.cscm.2017.03.005
3. Siddique, R., Klaus, J.: Applied clay science influence of metakaolin on the properties of mortar and concrete: a review. Appl. Clay Sci. **43**, 392–400 (2009). https://doi.org/10.1016/j.clay.2008.11.007
4. Murat, M., Comel, C.: Hydration reaction and hardening of calcined clays and related minerals. III. Influence of calcination process of kaolinite on mechanical strengths of hardened metakaolinite. Cem. Concr. Res. **13**, 631–637 (1983)
5. Moodi, F., Ramezanianpour, A.A., Safavizadeh, A.S.: Sharif University of Technology Evaluation of the optimal process of thermal activation of kaolins. Scientia Iranica **18**, 906–912 (2011). https://doi.org/10.1016/j.scient.2011.07.011
6. Cyr, M., Trinh, M., Husson, B., Casaux-Ginestet, G.: Effect of cement type on metakaolin efficiency. Cem. Concr. Res. **64**, 63–72 (2014). https://doi.org/10.1016/j.cemconres.2014.06.007
7. Tironi, A., Castellano, C.C., Bonavetti, V., Trezza, M.A., Scian, A.N., Irassar, E.F.: Blended cements elaborated with kaolinitic calcined clays. Proc. Mater. Sci. **8**, 211–217 (2015). https://doi.org/10.1016/j.mspro.2015.04.066
8. Ménétrier, D., Jawed, I., Skalny, J.: Effect of gypsum on C3S hydration. Cem. Concr. Res. **10**, 697–701 (1980)
9. Quennoz, A., Scrivener, K.L.: Interactions between alite and C3A-gypsum hydrations in model cements. Cem. Concr. Res. **44**, 46–54 (2013). https://doi.org/10.1016/j.cemconres.2012.10.018
10. Avet, F., Scrivener, K.L.: Hydration study of limestone calcined clay cement (LC3) using various grades of calcined kaolinitic clays. In: Calcined clays for sustainable concrete, pp. 35–40 (2018)