Development of a New Rapid, Relevant and Reliable (R^3) Testing Method to Evaluate the Pozzolanic Reactivity of Calcined Clays

F. Avet, R. Snellings, A. Alujas and K. Scrivener

Abstract This paper introduces a new rapid, relevant and reliable (R^3) test to characterize the pozzolanic reactivity of calcined clays. This test uses isothermal calorimetry to evaluate the reactivity by monitoring the heat release in portlandite/calcined clay/limestone model systems. Once the mix design was adjusted, a wide range of calcined clays was investigated. Tests were first run at 20 °C. Good correlations were found between the heat release at 6 days and the compressive strength results on mortar blends containing calcined clays and limestone. Another series of tests were carried out at 40 °C, enabling the isothermal calorimetry test duration to be reduced from 6 to 1 day, while keeping good correlations with strength results.

1 Introduction

The use of calcined clays as clinker substitute is a promising approach in order to decrease the economic and environmental costs of cement production, thanks to their wide availability and their high reactivity as pozzolanic material. Among the different kinds of clays, kaolinitic clays show the highest pozzolanic potential after calcination [1]. The calcination of kaolinite leads to the formation of the highly-reactive metakaolin phase, which then reacts during hydration to form C-A-S-H and in some cases, strätlingite [2]. To reach even higher clinker substitution levels, a coupled substitution with limestone can be used. The advantage of combining calcined clay and limestone is the enhancement of limestone reaction thanks to the

F. Avet (✉) · K. Scrivener
Laboratory of Construction Materials, IMX, EPFL, Lausanne 1015, Switzerland
e-mail: francois.avet@epfl.ch

R. Snellings
Sustainable Materials Management, VITO, 2400 Mol, Belgium

A. Alujas
CIDEM-UCLV, Universidad Las Villas, Santa Clara, Cuba

K. Scrivener and A. Favier (eds.), *Calcined Clays for Sustainable Concrete*,
RILEM Bookseries 10, DOI 10.1007/978-94-017-9939-3_67

aluminate provided by the metakaolin. This synergetic effect of calcined clay and limestone leads to the increase of the volume of hydrates formed. The feasibility of substituting half of cement by a combination of high-grade calcined clay and limestone has been demonstrated [3], but high-grade-kaolinitic clays are too expensive to be massively used in cement production. Therefore, a method to evaluate widely-available lower grade clays was investigated.

Several tests have been proposed to evaluate the pozzolanic reactivity of Supplementary Cementitious Materials. These tests are mostly based on portlandite consumption [4, 5]. However, they do not generally correlate accurately the mechanical properties of blended systems. This paper introduces a new rapid, relevant and reliable (R^3) method to evaluate the pozzolanic reactivity by monitoring the heat release during the pozzolanic reaction in portlandite/calcined clay/limestone mixes. This test was applied to a wide range of calcined clays and results were correlated to compressive strength results of mortars.

2 Materials and Methods

Seven different kaolinitic clays from various places around the world were used in this work. Their kaolinite content was determined by Thermogravimetric Analysis (TGA) from the water loss during kaolinite dehydroxylation. Since some calcined clays were not received completely calcined, the calcined kaolinite content was defined as the difference of the kaolinite content before and after calcination, as shown in Eq. 1.

$$\%\ \text{calcined kaolinite} = \%\ \text{kaolinite}_{\text{rawclay}} - \%\ \text{kaolinite}_{\text{calcinedclay}} \quad (1)$$

The physico-chemical properties of calcined clays are described in Table 1. The properties of clinker and limestone used for the mortar compressive strength tests are also described.

The results obtained on simplified systems of portlandite/calcined clay/limestone were compared to strength results of mortars. The different systems used for mortar testing are summarized in Table 2. Plain PC system was used as reference. Two

Table 1 Physico-chemical properties of calcined clays, clinker and limestone

Calcined clay	1	2	3	4	5	6	7	8	Clinker	Limestone
Origin of clay	NAm	SAs	SAm	SeAs	NAm	SAm	SAs	Quartz		
Calcined kaolinite (%)	95	79.4	66.2	50.8	38.9	35.0	17.0	0	–	–
D_{50} (μm)	5.1	5.3	4.0	10.9	8.5	23.5	5.9	11.2	8.4	7.2
Specific surface (m^2/g)	9.6	15.3	12.9	45.7	23.1	18.5	18.7	1.2	0.9	1.8

Origin of calcined clays *NAm* North America; *SAm* South America; *SAs* South Asia; *SeAs* Southeast Asia

Table 2 Composition of PC, PPC30 and LC^3-50 systems

	Clinker	Calcined clay	Limestone	Gypsum
PC	95	0	0	5
PPC30	65	30	0	5
LC^3-50	50	30	15	5

substitution levels were used: PPC30 refers to systems with 30 % of clinker substitution by calcined clays and LC^3-50 corresponds to systems containing 50 % of clinker and a combination of 30 % of calcined clay and 15 % of limestone and 5 % gypsum. Mortar bars were cast and tested mechanically according to EN 196-1 at 1, 3, 7, 28 and 90 days.

For the R^3 pozzolanic test, mixes containing portlandite and calcined clay were cast and the results of the tests were correlated to the strengths of PPC30 systems. Limestone was added to the mix for comparison with LC^3-50 blends strengths. The calcined clay to limestone ratio was fixed to 2:1 for the R^3 test. In order to reproduce similar reaction environment as in cement system, K_2O and SO_3 to calcined clay ratios were adjusted to 1/12 and 1/18 by mass, respectively. Moreover, the portlandite to calcined clay ratio was adjusted to 3/1 by mass in order not to run out of portlandite during the test. A water to solid ratio of 1.2 was used for all systems to ensure suitable workability and to provide excess water to the system for the reaction to keep occurring. The mix design was then applied to the different calcined clays, first at 20 °C. Then, 40 °C experiments were run in order get even quicker indication of calcined clay reactivity.

3 Results and Discussion

3.1 Strength Results

The compressive strength results for PPC30 and LC^3-50 are plotted as function of the calcined kaolinite content of calcined clay, as shown in Fig. 1. Dotted horizontal lines indicate the PC strengths at the different ages. Equivalent strengths to PC are obtained for blends containing only 40 % of calcined kaolinite from 7 days onwards. Thus, the use of low-grade clays still enables to get good results. Moreover, for each age, the strength linearly increases with the calcined kaolinite content of calcined clays. This demonstrates that the calcined kaolinite content is the dominant parameter determining the compressive strength results. Moreover, close strength values of PPC30 and LC^3-50 blends are obtained, especially at late age. The decrease of clinker content for LC^3-50 blends is thus compensated by the synergetic effect of calcined clay and limestone.

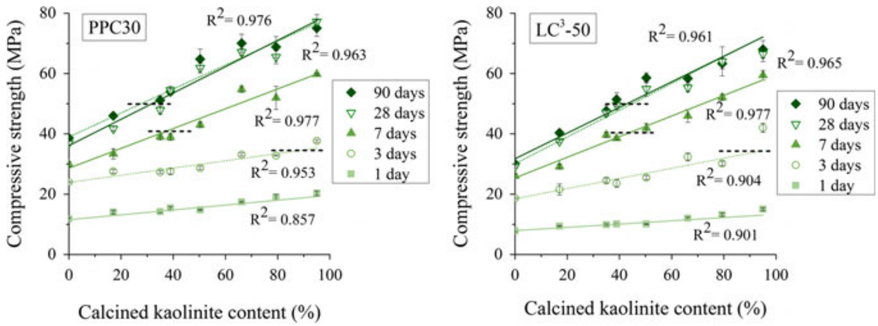

Fig. 1 Influence of the calcined kaolinite content on compressive strength results for PPC30 (*left*) and LC^3-50 (*right*) blends. *Dotted lines* indicate the PC strengths

3.2 R^3 Test Results at 20 °C

The cumulative heat normalized per gram of solid is shown in Fig. 2 for systems without and with limestone. The heat release globally increases with the calcined kaolinite content. The heat value at 6 days was chosen for the correlation to strength results, since the reaction stabilizes at this age. Figure 3 shows the correlations obtained are linear. Thus, the R^3 test is a valid way of characterizing the reactivity of calcined clays, since there is a globally good agreement with strength results.

3.3 Impact of Temperature

The increase of temperature from 20 °C to 40 °C of the isothermal calorimeter clearly accelerates the pozzolanic reaction, as shown in Fig. 4. The heat values after only 1 day at 40 °C are globally close to the heat values at 6 days at 20 °C. Thus,

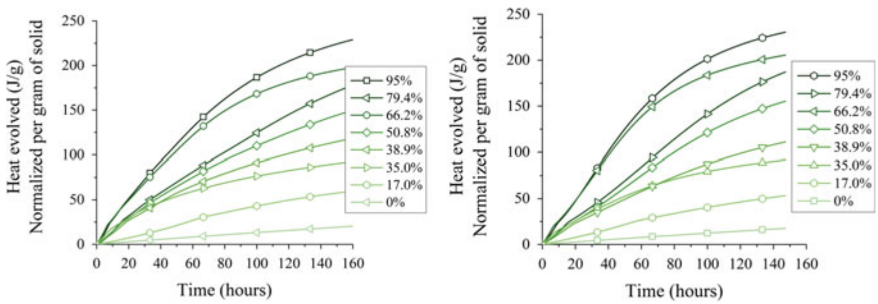

Fig. 2 Cumulative heat release of portlandite/calcined clay mixes without (*left*) and with (*right*) limestone at 20 °C

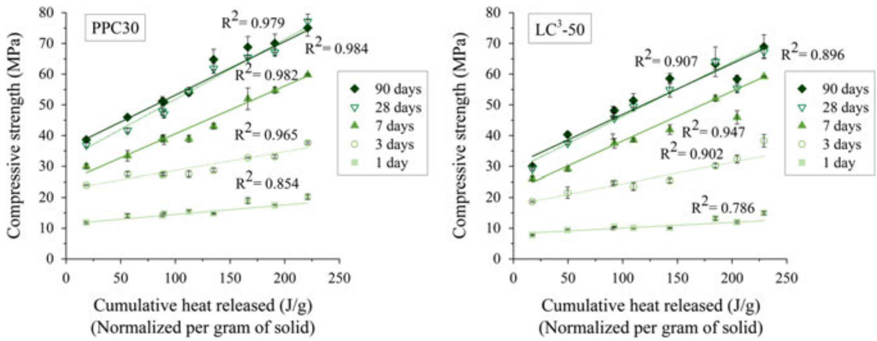

Fig. 3 Correlations of mortar compressive strength with the heat values at 6 days at 20 °C of portlandite/calcined clay mixes. PPC30 and LC^3-50 strengths are respectively compared with heat values of mixes without (*left*) and with (*right*) limestone

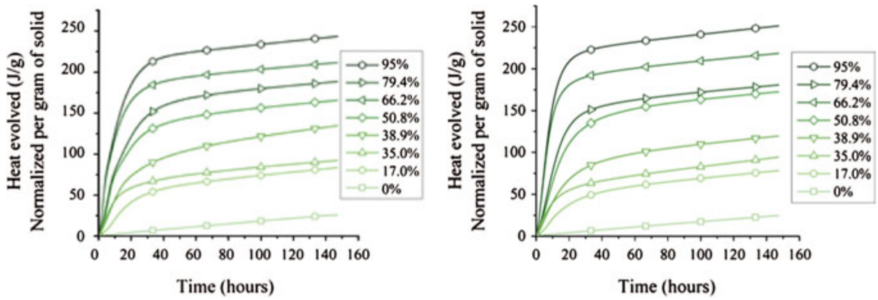

Fig. 4 Cumulative heat release of portlandite/calcined clay mixes without (*left*) and with (*right*) limestone at 40 °C

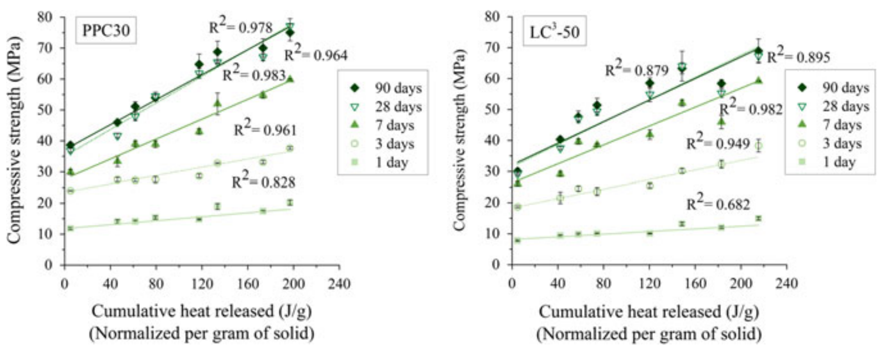

Fig. 5 Correlations of mortar compressive strength with the heat values at 6 days at 20 °C of portlandite/calcined clay mixes. PPC30 and LC^3-50 strengths are respectively compared with heat values of mixes without (*left*) and with (*right*) limestone

the correlation to compressive strength results was based on the 1-day heat values. Similar good linear correlations are found with strength results, as shown in Fig. 5. Thus, reliable indication on the reactivity of calcined clays can be obtained after only 1 day of testing.

4 Conclusions

This new R^3 pozzolanic test permits to get reliable indication of clay reactivity after 6 days of testing at 20 °C. For portlandite/calcined clay mixes without and with limestone, the heat release is linearly correlated to the compressive strengths of PPC30 and LC^3-50 blends. The test duration can even be reduced to 1 day by increasing the temperature of isothermal calorimetry to 40 °C. Correlations to compressive strength results are not significantly affected by this temperature increase.

Acknowledgments F. Avet and R. Snellings respectively acknowledge financial support by the Swiss Agency for Development and Cooperation (SDC) and the European Community under FP7-Marie Curie IEF grant 298337.

References

1. Fernandez, R., Martirena, F., Scrivener, K.L.: The origin of the pozzolanic activity of calcined clay minerals: a comparison between kaolinite, illite and montmorillonite. Cem. Concr. Res. **41** (1), 113–122 (2011)
2. Silva, P.S.d., Glasser, F.P.: Hydration of cements based on metakaolin: thermochemistry. Adv. Cem. Res. **3**, 167–177 (1990)
3. Antoni, M., et al.: Cement substitution by a combination of metakaolin and limestone. Cem. Concr. Res. **42**(12), 1579–1589 (2012)
4. Donatello, S., Tyrer, M., Cheeseman, C.R.: Comparison of test methods to assess pozzolanic activity. Cem. Concr. Compos. **32**(2), 121–127 (2010)
5. Tironi, A., et al.: Assessment of pozzolanic activity of different calcined clays. Cement Concr. Compos. **37**, 319–327 (2013)