ICSBE2016-97

REACTIVITY OF BLENDED SCMS FOR SUSTAINABLE TERNARY CEMENTS

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Abstract: The Cement industry is responsible for huge CO_2 emission; still, numerous efforts are being applied to increase the efficiency of cement plants. The CO_2 emissions from cement production can also be reduced by replacing clinker content with supplementary cementitious materials (SCMs). Ternary cements are one of the most efficient ways to reduce the clinker content up to 50% without affecting the performance of cement. Before replacing clinker with any of the SCM's, their reactivity must have to be studied properly. This paper will focus mainly on the reactivity of blended SCMs for ternary cements. Reactivity of different blends having calcined clay with limestone and fly ash with slag was studied in the presence of calcium hydroxide using isothermal calorimeter. The effect of different proportions of calcium hydroxide, accelerators, and temperature on reactivity was also studied. Additionally, the compressive strength of cement mortar cubes having 50% replacement of OPC was studied and further, the reactivity data of blends from calorimeter was compared with the compressive strength of mortars. It was observed that the compressive strength of calcined clay and limestone cement with different proportions was ranging from 38.17 to 32.70 MPa. Where as in the case of fly ash and slag cement having different proportions was ranging from 29.26 to 43.73 MPa. A reasonable good correlation was observed with the calorimeter energy data and strength.

Keywords: Ternary blended cements, Reactivity, Isothermal Calorimeter

1. **Introduction**

Cement production causes almost an equalling amount of CO2 emission. These emissions are mainly due to the decomposition of limestone during heating and the fuel required. However, some advancement in the field of improving the efficiency of cement plant are also done world wide, but still, this factor is found to be around 0.7 to 0.8 ton of CO2 emitted for 1 tone of cement production. Considering the facts of such huge emissions, but concrete made with cement is considered as cheapest and lowest associated CO2 material in comparison with other construction materials [1].

Considering the facts that cement industry is applying huge effort in reducing this huge CO2 emission still we need to look for the other available alternative. In the race of cement production, India comes on the second rank. This growth of infrastructure and industries is also forcing the cement industry to control on its CO2 emission. That is why pozzolanic portland cement come in the trend [2].

In India, around 65-70% of electricity is produced by coal-based thermal power plants which produce a huge amount of fly ash (FA). The abundant quantity of FA is available but due to its poor quality its utilisation is still limited in cement industry. An alternative for processing the FA by air separation or pre-grinding which can enhance its reactivity but at the same time such processes can increase the overall production cost.

Another type of waste material produced from iron industry is slag which is promising and valuable pozzolanic material especially for some specific durability requirements [3,4]. But its quantity is very limited and is specific. Due to its very small quantity available every single percent of slag is utilised in cement industry for producing Portland slag cement.

The third option comes as calcined clay based portland pozzolanic cement. But considering the facts of other useful applications of calcined clay such as in paint, paper and pharmacy industries, it was found to be uneconomical to use such clay made from high-quality fuel and pre-washed for removing impurities, as a perfect solution for the concern.

In such situation, ternary blended cements can be very helpful. Various countries have already standardised ternary blended cements. India also looking forward to the ternary blended cement based on FA and slag system named composite cement (CC)[5].

Another promising technique for producing ternary cement, limestone calcined clay cement (LC3) is also available. In this cement, lower grade quality clay needs to be used and because of this fact, this type of cement does not affect the present demand areas of calcined clay. In LC3, calcined clay gives pozzolanic behaviour in the presence of cement and limestone gives filler as well as synergic effect in the blended system [1,6,7].

Growth in cement development can be considered parallel to the demeaned. But at the same time, methods for testing these new cements are still the same. This seems to be a big loophole in the relation between cement technologies and methods for testing its reactivity properties [8,9]. The only major requirement in the usage of SCMs is the requirement of qualifying the test methods for their reactivity. Due to the recent development of ternary systems, the test methods available for the study of reactivity need to be designed in order to quantify the reactivity of SCMs blends. Methods that can be able to consider the pozzolanic as well as synergy effect of two blended SCMs together will be the futures for reactivity methods [9].

For this purpose, this study made an effort to develop a technique for the reactivity study of SCMs blended together. Due to the exothermic behaviour of pozzolanic reaction, an isothermal calorimetry-based technique was tried to develop. Similar techniques are already developed for calcined clay and limestone blended pozzolana but its knowledge is still limited with other SCMs combinations [8].

Similarly another study also made an effort to look the applicability of such technique for all the raw SCMs individually. However, still not clear which method can be used for a wide range of SCMs and their blends [9].

For this task, this study shows an effort in developing reactivity characterisation techniques for different blends combinations of SCMs. The reactivity of SCMs was studied in the presence of CH in different styles.

2. Materials

For the study, one type of kaolinitic calcined clay (K) blended with one pure limestone (LS) in different ratios and one pure dolomite (D) was used. For composite cement, one FA and one slag (S) were used in different ratios. The mix proportion of blends is given in Table 1.

Table 01. Blends mix proportions of SCMs

Blend	Ratio
B1 (Kaolinitic clay: limestone)	2:1
B2 (Kaolinitic clay: limestone)	1:1
B3 (Kaolinitic clay: limestone)	1:2
B4 (Kaolinitic clay: dolomite)	2:1
B5 (fly ash: slag)	2:1
B6 (fly ash: slag)	1:1
B7 (fly ash: slag)	1:2

All the raw materials were characterised for their chemical and physical properties as shown in **Table 2**. Particle size distribution (PSD) of all the raw materials was measured individually.

To make a uniformly homogenised blend of SCMs, a 5 kg capacity lab scale ball mill was used. At the same time, to avoid agglomeration 12.5 mm diameter balls were used. For making blended cements, clinker was ground in the lab to meet the specifications of a 43-grade ordinary portland cement as per Indian standard. That particular cement was then mixed with the blends in the dry form to make uniform blended cement. The proportion of clinker,

Table 2. Chemical and physical properties of raw

Constituents %	Kaolinitic calcined clay	Limestone	Dolomite	Fly ash	Slag
Los on ignition	3.03	36.96	46.90	1.11	0.32
SiO_2	53.53	11.02	0.75	58.82	32.26
Fe_2O_3	1.15	1.55	0.64	6.19	1.93
Al_2O_3	40.03	2.53	1.02	30.62	23.16
CaO	0.08	44.24	29.28	1.01	33.88
MgO	0.02	1.96	21.26	0.41	7.01
SO_3	0.12	---	---	0.12	Traces
Na_2O	0.24	0.50	---	0.19	0.34
K_2O	0.07	0.28	---	1.30	0.65
Mn_2O_3	---	---		---	0.30
Specific Gravity	2.64	2.64	2.65	2.26	2.87
PSD D(50)	5.86	11.1	11.1	37.3	12.2

SCMs and gypsum are given in **Table 3**. Homogeneity of the mixes was confirmed by visual observations.

3. Experimental work

3.1 Compressive strength test

All the blended cements were tested for compressive strength at the age of 1,3,7 and 28 days age. Water to cement ratio was kept 0.45 and was same for the blends. For this purpose, 7.06 cm cube was used as specified in Indian Standard. After casting, the cubes were stored for the first 24 hrs. in a temperature-controlled room at 27°±2 C. After demoulding, all the specimens were cured under water at the same temperature.

Table 3. Mix proportions of clinker and SCMs in ternary blended cements

Cement Type	Cement blend mix	C %	Blend %		G %
			SCM1	SCM2	
LC^3	B1 (K and LS	50	30.66	15.34	4
	B2 (K and LS)	50	23	23	4
	B3 (K and LS)	50	15.34	30.66	4
	B4 (K and D)	50	30.66	15.34	4
CC	B5 (FA and S)	50	30.66	15.34	4
	B6 (FA and S)	50	23	23	4
	B7 (FA and S)	50	15.34	30.66	4

Note: LC^3=Limestone calcined clay cement, CC= Composite cement, B= Blend K=Kaolinitic clay, LS=Limestone, D=Dolomite, FA=Fly ash, S=Slag, C= Clinker, G= Gypsum

3.2 Isothermal calorimeter

The isothermal calorimeter was used for recording the energy emitted during the pozzolanic reaction of blends in the presence of CH. This test was performed on the paste made with a water binder ratio of 0.6. The paste was mixed uniformly with the help of vortex mixer. The calorimeter study was done at 27° C for 3 days.

The energy evolved in blends was studied in three different styles. In the first set of experiments, blend and CH was kept 50%. In the second set, CH and blend were kept in 48.5%: 48.5% ratio and additional 3% of gypsum was also added. In the third and last set, the amount of CH was increased to provide more favourable conditions for the reaction and for that 3% of gypsum was added and the rest of powder was divided into 67%, 30% CH and blend respectively.

The energy-evolved results were normalised with respect to per gram of blend.

4. Results and discussion

4.1 Compressive strength

Average of compressive strength for 3 cubes is plotted in **Figure 1**, and presented in **Table 4**. It was observed that in the case of limestone calcined clay-blended cement strength gain was very fast. A clear difference was observed even at the age of 7 days. At 7 day it was found to be satisfying the Indian standard requirements for ordinary portland cement. This sudden increase in strength was found to be mainly because of calcined clay. Due to the fact the calcined clay was fine and the early strength gain was very high, a very little strength gain was found after 7 days. It was also noted that with an increase in the LS significant decrease was found. This phenomenon was found similar to the previous studies [6]. In the second type of blended cement containing dolomite (B4), some little difference in the strength with respect to B1 was observed. It was because of the fact that dolomite does not react, whereas LS reacts with aluminate from the clay and forms carboaluminates as a final product [4]. But another benefit came out from B4 blend was that the strength was not decreased due to the addition of dolomite into the system. It provides an additional application of dolomitic limestone, which is found unsuitable for the clinker production and usually considered as the burden over the limestone mines can be used for such types of cement blends.

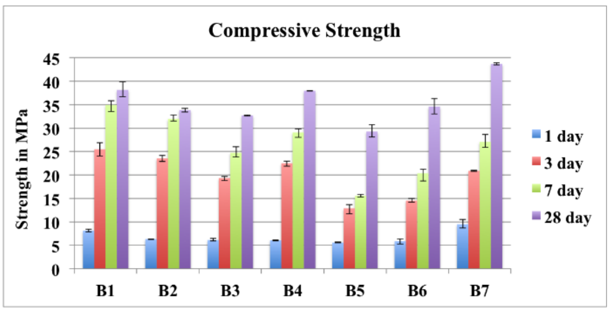

Fig. 1. Compressive strength at 1,3,7 and 28 days for all blended cements

In the third type of CC, B5 show low strength gain at all ages. This was because of the fact that FA reacts very slowly in the system and at the same time, the fineness was also comparatively coarse. The strength gain phenomenon is quite slow in case of FA pozzolanic reaction [3,4]. That is why the real strength data need to be observed at later ages. But still, by using a coarser FA and by interblending the cement, the 28-day strength was close to the requirements of PPC as per Indian standards. With an increase in slag percentage, a considerable increase was observed. If the slag content would have been further increased, the strength of cement can even match OPC. But due to the little availability of slag, it will not be fair to look for the blends contains high slag and lower FA. Additionally, this blending of FA and slag also increase the possibility of utilising the coarse and comparatively less reactive FA with good replacement levels. Surprisingly, even after replacing almost 50% of clinker, the strength of B1, B4, B7 blends was still equivalent to the 43-grade ordinary portland cement.

Table 04. Compressive strength in MPa at different testing age

Blends	1 day	3 day	7 day	28 day
B1	8.12	25.50	34.97	38.17
B2	6.13	23.53	31.96	33.84
B3	6.11	19.35	24.74	32.70
B4	6.02	22.5	29.07	37.98
B5	5.54	12.87	15.55	29.26
B6	5.89	14.51	20.34	34.57
B7	9.47	20.87	27.07	43.73

4.2 Energy recorded from calorimetry

Energy released from the reaction between SCMs blends and CH was recorded for the period of 3 days and was normalised with respect to the per gram of blend present for the reaction. Experimental data for the set 1 containing 50% CH and 50% blend plotted in **Figure 2,3 and 4**. It was observed clearly that clay blends give high energy in the beginning but FA blends started slower. In the second set, the effect of gypsum addition in the reaction was studied. In this case, an increase in the energy was observed. This was because of the fact that sulphates also take part in the reaction with the aluminate phase provided by the calcined clay and at the same time provides favourable conditions to accelerate the reaction [8]. Similarly, in the third set, even more favourable conditions were tried to provide by increasing the CH content into the system. In the third set of experiments, CH was increased because of the fact that in a pozzolanic reaction SCMs are found to be a barrier in the reaction of CH [9].

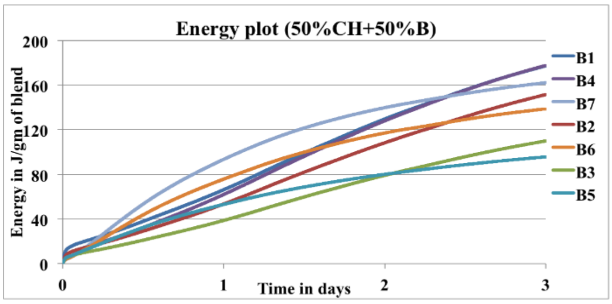

Fig. 2. Energy plot for calorimeter data in 50% CH and 50% blend condition.

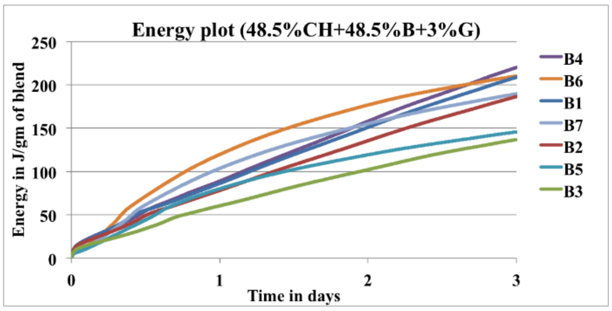

Fig. 3. Energy plots for calorimeter data in 3% gypsum, 48.5% CH and 48.5% blend

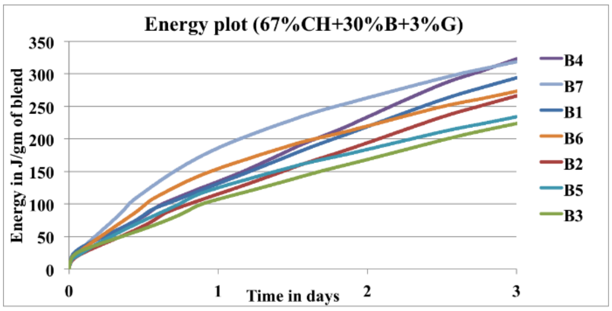

Fig. 4. Energy plots for calorimeter data in 3% gypsum, 67% CH and 30% blend

4.3 Strength vs Energy

To predict the strength of cement blend system, co-relation was calculated between energy evolved form calorimeter and compressive strength at 28 days. If 90-day strength needs to be compared with the energy data, then may-be just the 3-days data will not be suitable to be compared. This is because of the fact that in cement system almost total reaction will be finished by the period of 90 days. But in just 3-day reaction between CH and blend reaction cannot be considered as complete.

For 50 %CH and 50% blend, average co-relation was observed with the strength as shown in **Figure 5**. It was also observed that there was only on blend B7 that was not fitting the pattern to give good co-relation. For the second set of calorimetry experiments with additional gypsum almost no correlation was observed as given in **Figure 6**.

In the third set of experiment having more favourable conditions for reaction, it was observed that the co-relation was comparatively better than the set 1 experimental data as shown in **Figure 7**. Also, there is a possibility that the data recorded in the favour of acceleration of reaction can be correlated very well with the 90 or 180 days strength of mortar cubes.

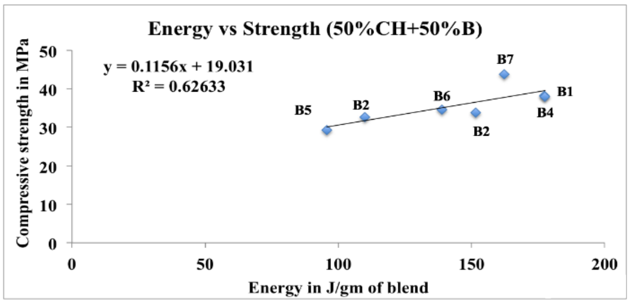

Fig. 5. Correlation between strength and energy for 50%CH and 50% blend

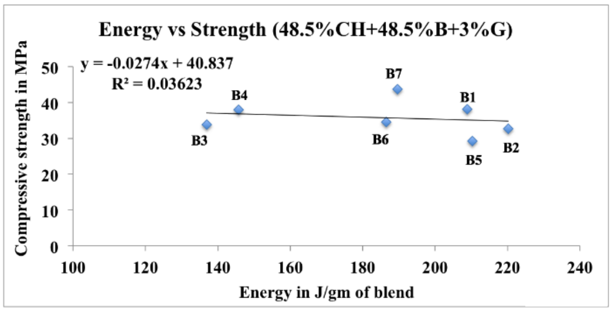

Fig. 6. Correlation between strength and energy for 48.5%CH, 48.5% blend and 3%gypsum

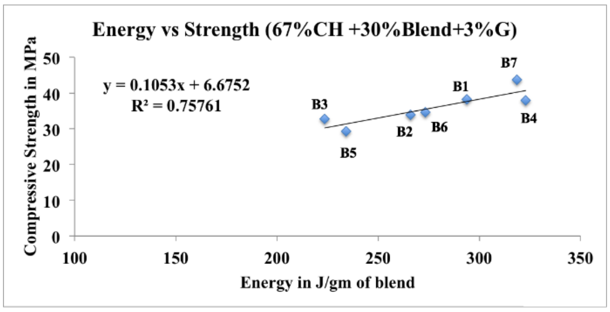

Fig. 7. Correlation between strength and energy for 67%CH, 30% blend and 3%gypsum.

1. Conclusions

Ternary blended cements especially in the case of limestone and calcined clay cement, a huge reduction in clinker content with a little compromise in strength was found to be a good option. In the case of fly ash and slag based cement the strength was slow and was obvious also due to the addition of FA.

Calorimetry data in CH and blend percentage of 67% and 30% with 3% gypsum was found to be suitable to predict 28 days strength excluding B7.

Further developments can be made for looking forward in the direction of co-relating 90 days or 180-days strength with such calorimetry techniques.

Acknowledgement

The authors would like to acknowledge Swiss Development Cooperation for funding "Low Carbon Cement- Phase 1" at IIT Delhi.

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