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outline some recent developments in the chemical activation of cements containing flyash.

CHEMICAL ACTIVATION OF FLYASH CEMENTS

Blended cements

Supplementary cementitious materials (SCM) used in blended cements are taken from either natural or waste sources. Examples of natural materials are volcanic ashes or limestone. Waste materials include slag (a byproduct from iron and steel manufacturing) and flyash (a residue from coal burning power plants).

Incremental use of flyash, slag and limestone as SCM helps to reduce the clinker factor, which in turn reduces CO_2 emissions from cement production. However, when the clinker portion is reduced, the cement typically suffers from lower

Table 1. Advantages and disadvantages of flyash as an SCM

Advantages	Disadvantages
Most abundant SCM worldwide (~700 million tpa)	Variable quality and performance
Pozzolanic activity contributes to cement hydration	Low early strengths, slower setting
High fineness and eventual post-mill addition allows narrower PSD and/or lower kWh/t	High fineness may increase water demand
Lower mill coating and better cement flowability	Potential for carbon staining
Allows lower specific CO_2 of finished cement	Potential adsorption of admixtures onto carbon

Table 2. Compositional analysis of OPC by Rietveld Analysis (QXRD)

Alite – Ca_3SiO_5	60.8%
Belite – Ca_2SiO_4	10.1%
Ferrite – $Ca_2(Al,Fe)_2O_5$	8.7%
C3A – $Ca_3Al_2O_6$ (cubic)	5.6%
C3A – $Ca_3Al_2O_6$ (orthorhombic)	1.5%
Periclase – MgO	1.9%
Portlandite – $Ca(OH)_2$	0.4%
Calcite – $CaCO_3$	1.4%
Gypsum – $CaSO_4 \cdot 2H_2O$	6.5%
Hemihydrate – $CaSO_4 \cdot 0.5H_2O$	0.4%
Arcanite – K_2SO_4	0.6%
Syngenite – $K_2Ca(SO_4)_2 \cdot H_2O$	1.0%
Aphthitalite – $(K,Na)_3Na(SO_4)_2$	1.2%

Table 3. Oxide analysis of flyash by XRF

SiO_2	53.9%
Al_2O_3	27.5%
Fe_2O_3	6.3%
CaO	2.0%
MgO	1.1%
SO_3	0.3%
Na_2O	0.4%
K_2O	2.5%
TiO_2	1.6%
P_2O_5	0.3%
SrO	0.1%
BaO	0.2%

Table 4. Compressive strength comparison of non-treated and 0.02% DEIPA-treated samples

		Compressive strength (MPa)		
	Air (%)	1 day	7 day	28 day
OPC – blank	1.9	23.2	50.2	na
OPC – 0.02% DEIPA	2.8	26.8	49.4	na
70% OPC + 30% FA – blank	2.7	13.3	32.9	43.6
70% OPC + 30% FA – 0.02% DEIPA	4.1	15.6	33.2	44.7

strength, notably at ages earlier than three days. Since flyash does not typically begin to react until after seven days, development of an accelerator is desired.

Flyash cement

Flyash is a widely used SCM for cement and concrete, and its application, as well as its advantages and disadvantages, are well known throughout the industry. The main advantages and limitations of using flyash are summarised in Table 1.

This article will present how ESE®, a series of additives offered by Grace that enable activation of cement and flyash hydration without the use of chloride or thiocyanate, partially offsets the negative effect of flyash on cement hydration. More specifically, it will discuss:

- To what extent and by which mechanism does ESE® allow a higher clinker replacement, while maintaining the same cement performance.
- How ESE® allows the usage of poorer performance clinker and flyash leading to a more consistent cement performance.

Quality improvers

For more than four decades Grace has been a leading provider of chemical solutions to improve the quality of blended cements. In particular, different chemicals, known as quality improvers are used to speed-up the binder-building process. This allows for set and rheology modification, and a faster development of strength in concrete.

ESE® cement additives

More than a decade ago, Grace introduced the ESE® series of additives based on diethanol-isopropanolamine (DEIPA) and ethanol-diisopropanolamine (EDIPA).[1] The ESE® technology frequently leads to superior concrete performance and higher clinker replacement in blended cements.

Recent studies have also shed light on the previously poorly-understood mechanisms that form the basis of the chemical activation, and provided evidence that flyash activation is indeed accelerated by ESE® additives. These additives provide performance benefits by several means:

- By enhancing the dissolution of the aluminate phases to accelerate the hydration of calcium sulfoaluminate phases.
- By changing the amount and morphology of portlandite.
- By changing the Ca/Si ratio of C-S-H.

- By accelerating the hydration of the flyash and slag phases.

Two studies have been reported by Riding *et. al.*[2,3] on how DEIPA and calcium chloride influence slag blended cement. This article will outline the mechanism of how DEIPA accelerates the hydration of OPC and flyash blended cement. The effect of aluminate dissolution and acceleration of cement hydration was monitored by calorimetry, mortar strength and XRD. The impact on the microstructure of the mortar, particularly the portlandite and flyash phases, was examined by SEM.

Test methodology

The QXRD of the OPC with BSA of 379 m^2/kg and XRF analysis of flyash with BSA of 290 m^2/kg used for this study are summarised in Tables 2 and 3. To make the flyash cement, 30 wt-% of flyash was blended with 70 wt-% of OPC in a V-blender. The samples were vacuum-packed in 450 g portions and stored until the EN-196 mortars were prepared. DEIPA was added with admixed water. After mixing of each EN-196 mortar, flow and plastic air tests were run and 50 − 60 g of the mortar was put in a calorimetric sample holder for heat flow measurement. The remaining mortar was then re-mixed by hand before being cast into the prism mold. The prisms were consolidated by a vibration table according to the EN-196 standard. Compressive strength tests were then performed at one, seven and 28 days of hydration. After the compression tests, the seven and 28-day samples were immediately soaked in isopropanol for at least 24 hours to stop hydration. The samples were then evacuated, impregnated in the epoxy resin (EPO-TEK OTE®) and allowed to fully harden for 24 hours at 40 °C. The hardened samples were next saw cut and polished using a 320 grit silicon carbide paper with ethylene glycol, followed by diamond abrasive powders of increasing fineness (9, 0.3 and 0.05 µm) immersed in polishing oil. The polished samples were then cleaned and carbon coated prior to examination under the SEM-EDX system.

For the XRD study, paste samples were made at a w/s ratio of 0.40. Then, 150 g of cement or cementitious materials was mixed with 60 g of water using an overhead mixer for four minutes. DEIPA was added to the cement with the mixing water. After mixing, the paste was poured into plastic molds to form cement paste cylinders with a diameter and height of 30 mm. The molds were sealed with parafilm and masking tape. Each mix filled three molds, one each for one, seven and 28-day XRD scans. The mixing and subsequent storage of the molds for the first 24 hours were performed in a lab set to 21 °C. To prevent bleeding or separation, the molds were placed in a sample rotator until 23.75 hours after mixing. At this time, all three samples were demolded. The seven and 28-day samples were placed in 21 °C lime water. The one-day sample was then cut into 3 mm wide disks using a wafering saw. The cutting saw was lubricated with polyethylene glycol, which was subsequently removed with isopropyl alcohol. The cleanest cut disk was then used for the XRD scans. XRD scans were generated with a PANalytical X'Pert Pro MPD using a Cu anode (45 kV, 40 mA) and a multi-strip detector. Data was collected in the range from 8 to 65 degrees 2-theta with a step size of 0.033 degrees/step for a total of 15 minutes, and then repeated an additional three times for a total of one hour.

Principal mechanism of action of ESE® cement additives

Figure 1 shows the comparison of heat flow curves between the blank and the treated sample with 0.02% DEIPA by weight of cement on OPC and flyash blended cement (containing 70% of the same OPC). In both cases, the second peak after the main silicate peak is increased, suggesting increased dissolution of the aluminate phases. This effect is more apparent in the flyash cement sample. The decrease of the portlandite phase with addition of

Figure 1. Heat flow curves with and without DEIPA in (a) OPC mortar and (b) flyash cement mortar.
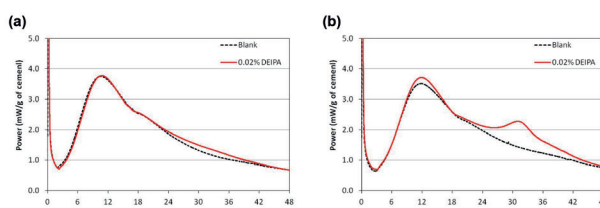

Figure 2. XRD patterns of the portlandite (~18˚ 2θ peaks) with and without DEIPA in (a) OPC mortar at seven days and (b) flyash cement mortar at one day.
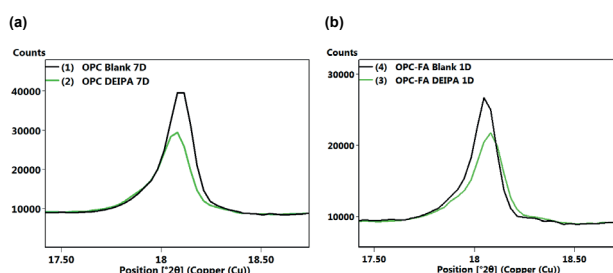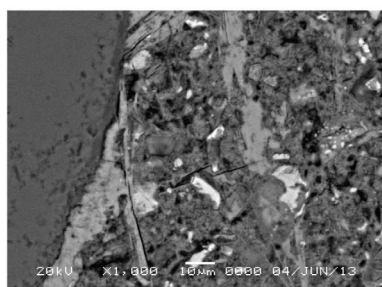
Table 5. **EDX analysis with and without DEIPA in at seven and 28 days**

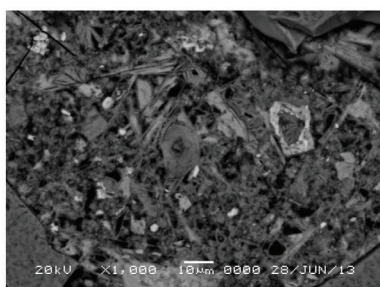|	7 days		28 days	
	Al/Si	Ca/Si	Al/Si	Ca/Si
OPC − blank	0.09	2.96	0.097	2.64
OPC − 0.02% DEIPA	0.09	2.96	0.098	2.82
70% OPC = 30% FA − blank	0.12	2.20	0.16	2.33
70% OPC + 30% FA − 0.02% DEIPA	0.15	2.87	0.17	2.12

Table 6. ESE® for flyash cements, case studies

Additive	Cement, country	Mill output	Early strengths	Late strengths	Application
ESE 100 @ 250 g/t	PO 42.5, East China	From 71 to 85 tph (+20%)	Same	Same	Increase 5% flyash
ESE 200 @ 300 g/t	PO 42.5, South China	From 160 to 180 tph (+12%)	Same	Same	Increase 5% flyash
ESE 300 @ 1000 g/t	CEM II/B-V, EU	N/A (blending station)	+2 MPa at 1 day (+18%) and +4 MPa at 2 days (+21%)	+4 MPa at 28 days (+9%)	Comply with internal quality specification
ESE 300 @ 1500 g/t	CEM IV/B (V), EU	N/A (blending station)	Same	Same	Increase flyash, produce special cement
ESE 400 @ 500 g/t	PPC, India	From 150 to 168 tph (+12%)	+3 MPa at 1 day	+4 MPa at 28 days	Offset variable flyash quality and clinker pre-hydration

Figure 3. SEM micrographs with and without DEIPA at seven days in OPC mortar.
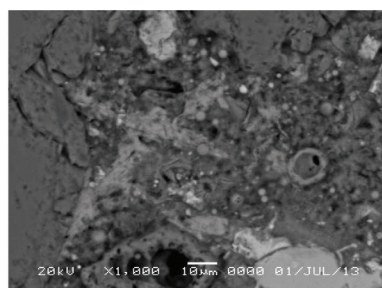
OPC - blank   **OPC with DEIPA**

Figure 4. SEM micrographs with and without DEIPA at seven days in FA and OPC mortar.

FA + OPC - blank   **FA + OPC with DEIPA**

0.02% DEIPA can be seen in the XRD patterns shown in Figure 2. Rietveld quantitative analysis of the XRD patterns also shows an increase in the AFt amount by 1.4% for the DEIPA samples at seven days for the OPC and at one day for the flyash cement. The consequent increase in strength at one, seven and 28 days is shown in Table 4. At one day, 0.02% DEIPA increased compressive strength by 3.6 and 2.3 MPa for the OPC and flyash blended cement, respectively. By 28 days, 0.02% DEIPA increased strength of the flyash blended cement by 1.1 MPa over the blank.

To understand why DEIPA leads to strength enhancement, SEM studies were performed to examine the microstructure of
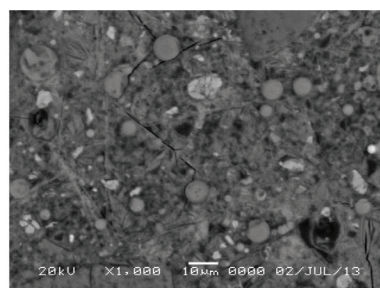
the mortar. Figure 3 shows the comparison of the blank and the 0.02% DEIPA OPC mortar at seven days. It can be seen that in the cement treated with DEIPA the portlandite crystals are showing more commonly, but not exclusively, as smaller randomly orientated and elongated needles preferentially located within the main cement paste, instead of larger hexagonal plates developing preferentially along aggregate boundaries. In the 28-day sample, this difference is less pronounced. An elemental analysis shown in Table 5 of the C-S-H phase in the OPC shows the Al/Si ratio between the blank and DEIPA to be similar at seven and 28 days, but the Ca/Si ratio of the 28-day sample to be higher in the sample containing DEIPA. This implies that there is more calcium in the C-S-H at 28 days in the DEIPA-OPC sample. It is not clear from this study if this increase is due to the incorporation of portlandite in the C-S-H or to a different C-S-H with a higher Ca/Si ratio.

In the flyash cement (Figure 4), changes were also observed in the amount and morphology of the portlandite crystals as compared to the OPC system. In this case, the Ca/Si ratio shown in Table 5 is much higher at seven days for the DEIPA sample, but the ratio reverses at 28 days. The reason for the reversal is not clear from this study. The SEM also shows less finer-sized flyash material and more hydration products in the DEIPA containing sample, indicating that DEIPA accelerates the hydration of not only the Portland cement component, but also the flyash particles. It is also interesting to see an increase of the AFt phase for the flyash cement even at one day in the presence of DEIPA. This observation is in line with the higher aluminate dissolution from the calorimetry of the flyash cement, suggesting that the DEIPA dissolves more aluminate to form an AFt phase. The XRD result also

shows a smaller portlandite peak in the sample with DEIPA (Figure 2b), suggesting that the change in portlandite occurs within the first day of hydration.

Case studies

The ESE® series of additives have been successfully used by cement plants around the world for more than a decade to achieve many benefits including increased mill output, increased use of SCM and increased use of poorer grade raw materials. Four field applications on flyash cements are outlined below to highlight these benefits. A summary for each case is shown in Table 6.

Case studies: China

Two ESE® additives were successfully applied in the production of flyash cements in China, in plants belonging to different groups. In the first plant, in Eastern China, ESE® 100 was dosed at 250 g/t of cement (PO 42.5, according to GB175 standard). Its addition at constant fineness (3300 cm^2/g and 0.7% residue at 80 μm) allowed the plant to increase mill output by 20% (from 71 to 85 tph) and add 5% more flyash in the cement while maintaining the same compressive strengths (25 MPa at three days and 49 MPa at 28 days) and setting time (IST 190 min, FST 280 min).

In a similar application at a South Chinese cement plant, ESE® 200 was dosed at 300 g/t of PO 42.5 cement, and allowed, at constant characteristics (Blaine 3500 cm^2/g, IST 160 min, FST 230 min, 29 MPa at three days, 52 MPa at 28 days), an increase of flyash addition to the cement by 5% compared to the blank cement. Mill output was also increased by 12% (from 160 to 180 tph).

Case study: EU

ESE® 300 was successfully implemented in a European blending plant (CEM I interblended with flyash), and used at two dosages for producing two types of flyash cements. The ESE® 300 at 1000 g/t was used to produce a CEM II/B-V 42.5N with 27% flyash, while still allowing the plant to comply with stringent strength requirements at all ages in the internal specifications. Strengths, compared to blank cement, were enhanced by the ESE® 300 from 11 to 13 MPa at one day, from 19 to 23 MPa at two days and from 46 to 50 MPa at 28 days (respectively +2, +4 and +4 MPa). Interestingly, the same additive was also used at 1500 g/t in the same blending station, and allowed the production of a CEM IV/B (V) 32.5R for special applications. In this case the activation of the flyash/cement system allowed the increase of flyash content to 45%, while still complying with internal and external specifications on setting time and strengths.

Case study: India

Finally, ESE® 400 was successfully adopted in an Indian plant, producing PPC cement according to IS standard, with 34% flyash. In this application the ESE® was able to provide a 12% mill output increase (from 150 to 168 tph) at constant fineness. Clinker replacement was not attempted in this case as the flyash content was already close to the upper limit allowed by the standard. More

significantly, the ESE® was able to provide a sufficient chemical activation of the clinker-flyash system, such that it was possible to use different grades of flyashes and clinkers in different states of prehydration, especially during the monsoon season. This allowed the plant to maintain a significantly reduced deviation of cement strengths, increasing internal compliance from 60% to 85 – 90%, therefore meeting both internal and official standard requirements, while still allowing the use of variable amounts of low quality flyash batches and prehydrated clinkers.

Conclusion

DEIPA accelerates the early and late strength hydration of Portland cement and flyash blended cements by:

- Enhancing the dissolution of the aluminate phases to accelerate the hydration of calcium sulfoaluminate phases.
- Changing morphology of portlandite from massive hexagonal plates along aggregate boundaries to smaller randomly orientated and elongated needles located preferentially within the main cement paste.
- Decreasing the amount of portlandite, while increasing the Ca/Si ratio of C-S-H.
- Accelerating the hydration of the flyash particles.

The ESE® technology was successfully commercialised in different plants across the world, and facilitated the production of flyash cements with higher performance (at the same cost) or lower cost (at the same performance). The chemical activation (and the grinding aid contribution) provided by the ESE® allowed different possible uses of the additive, such as:

- Increased flyash (decreased clinker) without sacrificing cement performance, hence reducing cost/MPa.
- Increased cement strength to comply with specifications.
- Production of special cements for high-value niche applications.
- Mitigating the effect of variable flyash quality and variable activity of clinkers in different states of prehydration on cement performance. 🌐

References

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