Mechanochemical Technology: Synthesis of Energetically Modified Cements (EMC) with High Volume Fly Ash Content

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Abstract

Energetically Modified Cement (EMC) consists of mechanochemical processed blend of ordinary Portland Cement (OPC) and pozzolan by multiple high intensity grinding mills to increase surface activation of the OPC and pozzolan particles. Fly ash of low reactivity was selected for activation as pozzolan.

Performance of EMC with 50%-70% fly ash is compared to OPC and simple blends of OPC and fly ash as binder in mortar and concrete in terms of setting time, strength development, drying shrinkage, sulphate resistance and alkali-silica reactivity. Strength of EMC with 50% fly ash is comparable to OPC, setting time is similar, and alkali-silica reactivity and drying shrinkage are lowered.

Environmental benefits are activation/use of fly ash that was not suitable for addition to concrete, reduced CO_2 emission to the atmosphere by using much less cement clinker, and reduced energy consumption in the concrete binder production.

1. Introduction

The energetically modified cement (EMC) technology was developed at Luleå University of Technology in Luleå, Sweden, by Dr. Vladimir Ronin *et al.* in the early 1990's. The EMC technology employs a high intensity mechanical activation process to increase the reactivity of Ordinary Portland cement (OPC) with high filler and/or pozzolan replacements. The EMC technology consists of processing a blend of OPC and filler/pozzolan through multiple high intensity grinding mills to impart increased surface activation of the OPC and pozzolan particles. The high intensity grinding is typically accomplished by multiple stages of vibratory or stirred ball mills. The grinding circuit and type of grinding mills are typically custom designed for the raw materials to produce EMC low in Portland clinker with performance characteristics equivalent to parent OPC, or to make EMC with similar clinker content and superior properties. The process can also be used to activate pozzolans of low reactivity (like certain fly ashes) and used them as addition to the concrete mixer later on.

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A number of EMCs, and concrete based on them, has been tested at Luleå University of Technology (e.g. [1]-[9]) as well as at SINTEF (e.g. [10] and [11]) both for performance and microstructural changes to understand mechanism.

A recently developed energetically modified product is fly ash with ≈5% cement treated in the vibration mill that can be added together with Portland cement in the production of a concrete in a conventional mixer. It has been shown that the amount of fly ash can be increased from about twenty percent with untreated fly ash to the level of seventy percent with modified fly ash maintaining the required strength level. A commercial product with energetically modified fly ash (EMFA) has been introduced in Texas, USA, under the trademark CemPozz, and it is this product that has been used in the present investigation under the abbreviation EMFA. One interesting field observation using concrete produced with EMFA was that there seems to be significantly less appearance of cracks when producing slabs on ground and highway paving in comparison with the general experience using traditional concretes.

2. Experimental

The material used in the major part of this study is a 50:50 inter-grind (EMC) of TXI-Ordinary Portland cement (OPC) and Reliant Energy's Limestone Power Station fly ash (FA). The physical and chemical characteristics of the EMC are compared to that of OPC, FA and a conventional 50:50 blend of OPC and FA, while the EMC performance in mortar and concrete is compared to that of neat OPC and OPC with 50% FA replacement.

Chemical analyses have been performed according to ASTM D-4326 and ASTM C-114 while the particle size distributions of EMC cement and the constituent raw materials (OPC and FA) have been performed with the use of Hariba laser scattering particle size analysis.

Time of setting of EMC paste were compared to that of reference OPC paste using the Gilmore apparatus according to ASTM C-266. The paste consistency was verified using the Vicat needle per ASTM C-187. Evaluation of water demand and compressive strength development of mortar and concrete has been made in accordance with ASTM C-109, ASTM C-311 and ASTM C-192. Sulfate resistance was evaluated according to ASTM C-1012, while alkali silica reactivity (ASR) was tested per ASTM C-441.

Paste samples for DTA/TG (Differential Thermal Analysis/Thermo Gravimetry) were crushed to a fine powder and dried at 105°C (i.e. to remove physically adsorbed water). The DTA/TG experiments were carried out by a NETZSCH 409 STA with a heating rate of 10 °C/min until 1000°C and nitrogen as a carrier gas. The sample (≈ 150 mg) was contained in an alumina crucible and alumina powder was used as a reference. The accuracy of the temperature determined for phase transitions was within ±2°C, while the accuracy of the mass losses was within ±0.3 mg.

Paste samples for MIP/HeP (Mercury Intrusion Porosimetry/Helium Pychnometry) were bits of about 5 mm size. The MIP experiments were carried out with the Carlo Erba Porosimeter (Model 2000) that records the pore size (radii) distribution of the sample between 5 and 50,000 nm, assuming cylindrical pores. The density of solid materials, ρ_s, was determined by Micrometrics AccuPyc 1330 He-pycnometer, while the particle density, ρ_p, was determined by Carlo Erba Macropores Unit 120. The accuracy of total porosity is within ±0.5 and density within ±0.01 units.

3. Results and discussion

The chemical analysis of EMC and its constituents are listed in Table 1 and corresponding particle size distributions in Table 2. The chemical analysis corresponds to an ASTM Class F fly ash. The EMC grinding process was effective in reducing the coarse fraction of the fly ash. The percentage of the simple blend retained on 325 Mesh was decreased from 12% to 5% by EMC method. This specific type of fly ash is relatively coarse and has significantly lower pozzolanic activity as compared to the other ashes in the area. Another study of EMC using 50% ASTM Class F fly ash (noted AFP for chemical analysis in Table 1) replacement [4] up to 28 days curing revealed that fine particles of fly ash and cement formed agglomerates of outer size comparable to cement grains but with a considerable inner surface explaining increased reactivity. The results for these samples [4] including analyses after 2.5 years (50/50 sealed/wet cured) are listed in Tables 3 and 4 for TG and porosimetry, respectively. EFAP denotes energetically modified 50/50 OPC/FAP paste, while BFAP is 50/50 OPC/FAP blended paste.

Table 1. Chemical composition of EMC (50/50 OPC/FA)
and its constituents, as well as fly ash for TG and porosity test (FAP)

Compound	OPC	FA	EMC	FAP [4]
CaO	62.4 %	15.0 %	40.9 %	2.5 %
SiO_2	17.8 %	49.4 %	33.2 %	53.0 %
Al_2O_3	4.0 %	19.6 %	6.3 %	25.0 %
Fe_2O_3	3.9 %	5.2 %	4.1 %	9.5 %
SO_3	3.2 %	0.8 %	1.6 %	-
Na_2O	<0.1 %	0.3 %	0.1 %	-
K_2O	0.3 %	1.2 %	1.2 %	-
Insolubles	0.5 %	51.3 %	21.6 %	-

Table 2. Particle size distribution

Parameter	OPC	FA	50/50 Blend	EMC
Median size (µm)	16.0	14.3	14.3	11.8
Min. size (µm)	1.5	1.3	1.3	1.5
Max. size (µm)	50	100	100	70
Specific surface (cm^2/cm^3)	5,624	6,624	6,075	7,220
< 10µm (%)	61	38	52	63
> 325 Mesh (%)	5	20	12	5

Table 3. Features from thermal analysis for EFAP/BFAP paste as a function of time.

Age	Total mass loss (%)	Degree of hydration (%)	CH (%)	CH/mass loss (%)
6 h / 12 h	6.89 / 7.30	28 / 29	4.11 / 3.90	60 / 53
1 day	8.64 / 7.96	69 / 64	8.65 / 6.92	100 / 87
3 days	9.93 / 9.73	79 / 78	9.28 / 8.67	93 / 89
7 days	10.38 / 10.20	83 / 82	9.18 / 8.62	88 / 85
28 days	11.15 / 10.89	89 / 87	7.37 / 8.25	66 / 76
910 days	13.46 / 14.27	108 / 114	3.99 / 5.78	30 / 41

For the EFAP and BFAP pastes in Table 3, the total mass loss is only marginally higher for EFAP than for BFAP at the different termini, except for 910 days when it actually lower probably due to a denser matrix halting reaction. The CH content reaches a higher level in EFAP than in BFAP at 1 day, but decreases faster as a function of time and reaches a lower level at 28 days. This indicates that the pozzolanic reaction of fly ash is faster in EFAP (already between 1 and 3 days) than in BFAP (mostly between 7 and 910 days), which is understandable considering that spherical shells in the fly ash are crushed in the milling process allowing simultaneous reaction on two sides of the glassy fly ash wall. The consumption of CH in EFAP paste is significantly more than in BFAP paste after 28 and 910 days, being +13% and +27%, respectively.

The general usual trends in Table 4 are that the porosity decreases as a function of time and the specific surface increases as a function of time as the pores becomes smaller in size but higher in numbers (e.g. gel pores). The average density of solids decreases as a function of time due to increasing amount of crystal water as hydration proceeds. The porosity of EFAP paste is smaller than the blended BFAP paste from about 7 days due to higher degree of hydration/pozzolan reaction, and is particularly much lower after 910 days. SEM images of 7 days paste in Fig. 1 show that the EFAP paste appears much denser than BFAP paste. The pore size distribution of the two samples plotted in Fig. 2 reveals a substantial pore refinement with the average pore openings of EFAP and BFAP being

11 and 22 nm, respectively. The pore size distribution is very different; whereas BFAP has a bimodal size distribution of pore openings with a considerable amount around 600 nm and the rest below 100 nm. EFAP, on the other hand, has only a small amount of pores with openings above 40 nm. The reason why $\varepsilon_{Hg} > \varepsilon_{He}$ in particular at 910 days (see Table 4) is probably that highly pressurized mercury are crushing delicate structures and opens otherwise inaccessible pores (reason for strange S_g?)

Table 4. Specific surface, S_g, particle density (ρ_p), solid density (ρ_s), mercury accessible porosity (ε_{Hg}) and helium accessible porosity (ε_{He}) of EFAP / BFAP pastes as a function of curing time.

Age	**S_g (m^2/g)**	**ρ_p (kg/m^3)**	**ρ_s (kg/m^3)**	**ε_{Hg} (vol%)**	**ε_{He} (vol%)**
6 h /12 h	8.4/9.7	1,300/1,231	2,588/2,519	48.2/47.7	49.8/51.1
1 day	20.0/15.5	1,302/1,243	2,373/2,359	43.7/44.7	45.2/47.3
3 days	32.8/22.7	1,349/1,313	2,264/2,260	39.3/38.4	40.4/41.9
7 days	30.6/20.7	1,377/1,383	2,235/2,248	37.6/35.9	38.4/38.5
28 days	40.2/27.2	1,349/1,371	1,931/2,102	31.7/34.7	30.1/34.8
910 days	35.7/44.7	1,324/1,180	1,609/1,856	23.2/40.5	17.7/36.4

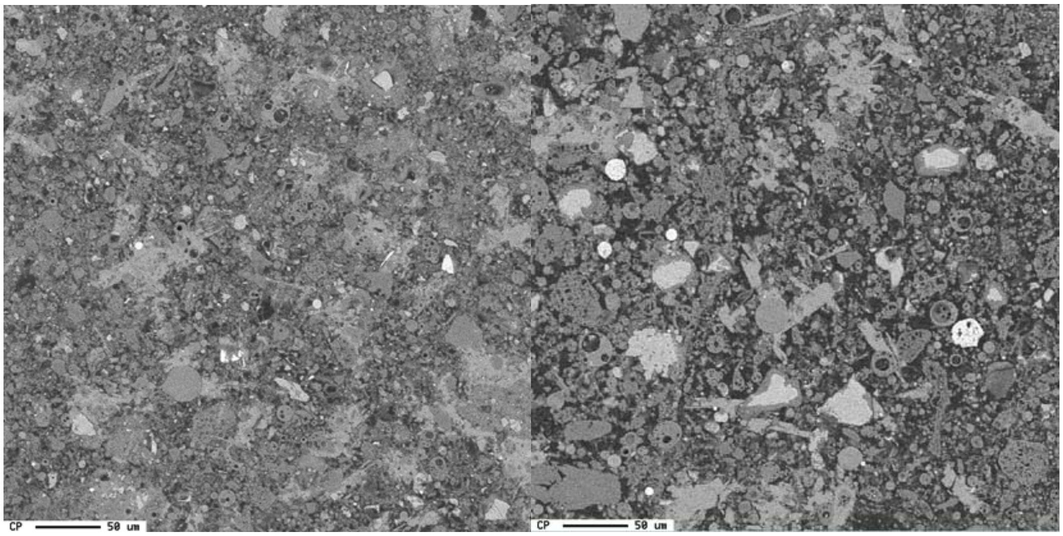

Fig. 1 Backscattered electron images (250x) of EFAP (left) and BFAP (right) pastes cured for 7 days at 20°C. The matrix of BFAP appears more porous than the matrix of the EFAP paste, and there are more unreacted cement grains in the BFAP paste. The light gray areas of calcium hydroxide seems to be mass like in EFAP paste, and a mix of mass like and larger individual crystals in the BFAP paste (probably a matter of available space).

The setting behavior of EMC paste is very similar to that of the reference OPC, as can be seen from Table 5. Conventional high volume fly ash (HVFA) portland-pozzolan blended cements, on the other hand, have typically longer set time; 3-5 hours for initial set and 5-7 hours for final set.

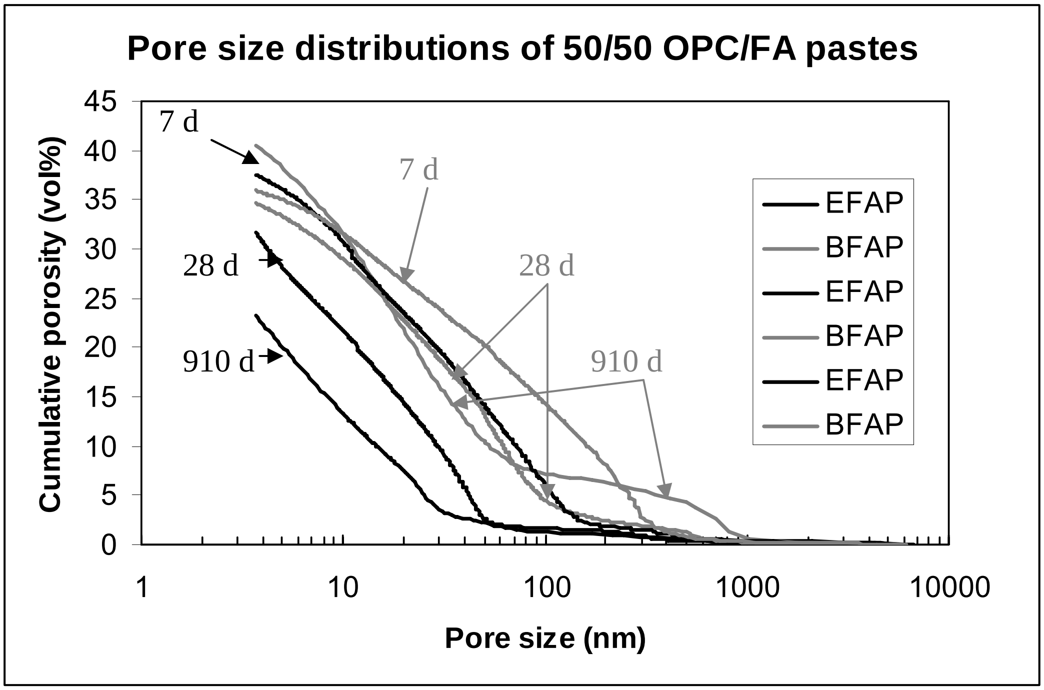

Fig. 2 Pore size distribution in EFAP and BFAP pastes at 7, 28 and 910 days.

Table 5. Time of Setting of Paste of OPC and EMC (50/50 OPC/FA)

Property	OPC	EMC
w/cm	0.24	0.22
Initial Set Time (hours:min)	2:29	2:26
Final Set Time (hours:min)	3:33	3:41

Table 6 represents the data for water demand and the compressive strength development of mortars based on EMC cement (30, 50 and 70% FA) in comparison with ordinary Portland cement and ordinary Portland cement with 20 and 40% of replacement with FA that has not been subjected to the EMC process (reference blends). EMC with 30% fly ash and water-to-cementitious material ratio (w/cm) 0.40 can be considered as high strength / high performance alternative for the newly developed blended cements, while 70% FA replacement may consider a high performance HVFA (high volume fly ash) cement.

According to Table 6, the EMC cement made by 50% OPC and 50% FA gave about 40% higher strength after 24 hours than the reference OPC. This EMC mortar had slightly lower compressive strength than OPC mortar at 7 days, but was superior to OPC mortar after 28 days. The EMC (50 % FA) performed significantly better than portland-pozzolan blended cements with 20% and 40% fly ash replacements. The workability of this EMC appears better than the OPC. The high fly ash content in combination with optimized particle size distribution allows 10% reduction in w/cm, which along with the increased reactivity of FA contributes to higher long-term strength. The EMC based on 30% FA and 70% of OPC had compressive strength evolution in line with rapid hardening Portland cement and gave a 28 days flexural strength of 9.6 MPa.

Table 6. Compressive Strength Development (MPa)

Cement type	**w/cm**	**Curing time (days)**			
		1	**3**	**7**	**28**
OPC[1]	0.48	10.3	26.6	30.0	38.6
EMC (50 % FA)[1]	0.43	14.7	22.9	27.2	41.1
EMC (30 % FA)[1]	0.40	36.7	-	51.6	62.4
EMC (70% FA)[2]	0.42	11.0	23.0	28.0	-
EMC (70% FA)[2]	0.38	12.5	23.4	30.0	-
80 % OPC[1]+20 % FA	0.46	6.5	20.4	23.6	35.8
60 % OPC[1]+40 % FA	0.44	3.8	15.1	17.7	29.6

[1] OPC from Texas, USA. [2] OPC (CEM I 42,5) from Sweden

The setting time of HVFA EMC (70% FA) is in line with OPC; initial and final set 2 h 40 min and 3 h 50 min, respectively. No water reducing agent has been used for the mortar with w/cm = 0.42 in Table 6. It had 10-12% higher flow than OPC mortar with same water content. HVFA EMC is very sensitive to addition of superplasticizer. Only 0.1% by mass of cementitious material (cm = OPC + FA) leads to a reduction of w/cm from 0.42 to 0.38 while maintaining flow. Mortars with HVFA exhibit excellent surfaces without flaws. According to Table 6, HVFA EMC shows improved 1 day strength and comparable 7 days strength to OPC mortar of comparable flow.

The EMC strength development relative to OPC was also evaluated using concrete cylinders as shown for the recipes in Table 7 and compressive strengths in Table 8. Even though the earlier compressive strength of EMC concrete was 10-14% lower than OPC concrete, the 28 days strength was 11% higher.

Table 7. Concrete mix design parameters

Parameter	OPC	EMC (50% FA)
Cement (% of mass)	13	13
Sand (% of mass)	38	38
Coarse aggregate (% of mass)	45	45
w/cm	0.67	0.66
Slump (mm)	50	50
Air content (vol%)	2.0	1.5
Unit weight (kg/m^3)	2,357	2,447

Table 9 represents the change in length of mortar bars exposed to sodium sulfate solution and the maximum permissible values for specimens. Total six specimens for each type of cement have been tested. The mortar bars made with EMC cement (50% FA) have slightly improved sulfate resistance over reference OPC. The expansion after 4 weeks was roughly one fourth of the maximum permissible level for blended cement. Table 9 also shows that mortar bars made with EMC cement have considerably better resistance (92% improvement) with respect to alkali-silica reactivity (ASR) than OPC mortar bars.

Table 8. Concrete strength development

	w/cm	Compressive strength (MPa)			
		3 d	7 d	14 d	28 days
OPC	0.67	16.0	22.1	26.4	29.0
EMC-50% FA	0.66	13.8	19.4	23.7	32.2
% of reference	-	86	88	90	111

Table 9. Expansion of mortar due to sulfate exposure and ASR

Sulfate resistance per ASTM C 1012 (% Δ-length)		
Cement	OPC	EMC (50% FA)
Max. limit (at 4 weeks)	0.012	0.041
Exposure for		
1 week	0.006	0.006
2 weeks	0.012	0.011
3 weeks	0.013	0.011
4 weeks	0.013	0.011
ASR per ASTM C 441 (% Δ-length)		
Cement	OPC	EMC (50% FA)
After 14 days	0.026	0.002 (-92%)

Table 10. Concrete mixtures using EMFA, their slump and compressive strength development (MPa).

EMFA (%)	35	50	50
OPC+EMFA (kg/m^3)	256	273	249
EMFA (kg/m^3)	93	136	125
Water (kg/m^3)	106	191	137
25 mm aggregate (kg/m^3)	1127	1097	1038
Fine aggregate (kg/m^3)	827	742	919
Air-entrainer (ml/m^3)	155	0	155
Water reducer (ml/m^3)	580	0	657
w/cm	0.40	0.70	0.55
Slump (mm)	44	216	152
7 days σ_c (MPa)	25.6	9.8	14.6
28 days σ_c (MPa)	33.8	19.9	26.2
56 days σ_c (MPa)	36.8	24.9	31.2

σ_c = compressive strength

Table 11. Concrete mixtures using EMFA, their slump and compressive strength development (MPa).

EMFA (%)	55	55	60	60
OPC+EMFA (kg/m^3)	273	273	249	243
EMFA (kg/m^3)	150	150	149	146
Water (kg/m^3)	136	158	132	148
25 mm aggreg. (kg/m^3)	1097	1097	1068	1038
Fine aggregate (kg/m^3)	823	848	854	825
Air-entrainer (ml/m^3)	0	0	155	116
Water reducer (ml/m^3)	696	1005	657	464
w/cm	0.50	0.58	0.53	0.61
Slump (mm)	140	165	133	171
7 days σ_c (MPa)	15.9	12.7	15.2	12.7
28 days σ_c (MPa)	27.6	24.7	26.0	23.6
56 days σ_c (MPa)	34.4	30.4	31.4	29.5

σ_c = compressive strength

In Texas, USA, a truck stop was made in October 2004 using concrete with 250 kg/m^3 cementitious material (40% OPC and 60% EMFA). The 28 day strength was 20 MPa and the surface excellent without cracks as indicated by the photos in Fig. 2. Laboratory experiments showing reduced drying shrinkage is reported elsewhere [12].

Later a part of Highway 69 in Texas was made by concrete with 50% OPC replacement by EMFA. The total cementitious material was 280-300 kg/m^3 and it achieved 15-20% higher 28 day strength than specified and 50% reduction in cracking compared to traditional pavement according to Texas Department of Transportation. Surface finish was excellent and reduced labour requirements. Some photos are shown in Fig. 3.

Fig. 2. Pouring concrete for the truck stop (left) and concrete surface of the truck stop after setting (right).

Fig. 3 Fresh (left) and hardened (right) concrete surface for Highway 69.

Regarding the energy consumption of producing EMC (50% FA) versus OPC, the following statements can be made: The manufacturing process of OPC consists primarily of quarrying or blasting of raw materials (limestone, clay), crushing, grinding, blending and conveying of the said raw meal to cement kilns where at high temperatures (about 1450 °C) the formation of Portland clinker takes place. The obtained clinker is further ground with gypsum to produce the final product Portland cement. EMC cement contains typically 50% of OPC and 50% of fly ash (FA). Production of such cement includes primarily grinding of FA to obtain fraction < 250 microns (if required), blending of the ground FA with OPC and processing of the said blend through EMC vibrating milling system to obtain the product with the similar size distribution as commercially available Portland cements (fraction < 150 microns). A comparison of the energies involved in the two processes is shown in Table 12, and one can see that the EMC with 50% fly ash only require 54% energy compared to OPC production. 50% OPC replacement should account for 50 % less CO_2, but since EMC require somewhat more electrical energy in grinding the saving may be about 40% (providing that the energy production involves burning of fossil fuel).

Table 12. Energy consumption OPC vs. EMC

Cement	OPC	EMC (50% FA)
Clinker production energy:	3.16 GJ/ton (878 kWh/ton)	1.58 GJ/ton (50% clinker)
Burning energy:	*100%*	*50%*
Electrical power grinding cement:	100 kWh/ton	(50% OPC) 50 kWh/ton
Electrical power EMC process:	0	38 kWh/ton
Electrical power:	*100%*	*88%* (38+50 = 88)
Total energy	(100%·878+100%·100) /(878+100) = *100%*	(50%·878+88%·100) /(878+100) = *54%*

4. Conclusion

EMC cement based on 50% of ASTM Class F fly ash (FA) and 50% of ordinary Portland cement (ASTM Type I)) showed about 40% higher compressive strength after 24 hours than the reference Portland cement. Compressive strength development for EMC at 7 and 28 days are in line with that of the pure ASTM Type I Portland cement.

The EMC (50 % FA) gave respectively about two times and three times the 1-day compressive strength of conventional blends of Portland cement with 20 and 40% replacement by ASTM class F fly ash. The 7 and 28 days compressive strength were also significantly higher.

EMC cement based on 30% of FA and 70% of Portland cement showed strength development in line with rapid hardening Portland cement, which enables production of high performance/ high strength FA concretes.

EMC (50 % FA) had less water requirements (increased workability) compared to simple blends, which contributes to higher strength along with the increased fineness**.**

The mortar samples produced with EMC (50 % FA) had improved sulfate resistance. The change of length values stood at just over 1/4 of the permitted level after 4 weeks and 1/10th of the permitted level after 15 weeks.

The mortar samples produced with EMC (50 % FA) had considerably lower alkali-silica reactivity (up to 92% lower change in length) in comparison with ordinary Portland cement.

Fly ash of low pozzolanic activity can be activated by the energetic modification technique (EMFA) together with a small amount of OPC (≈5%) and be used as a pozzolanic additive to mortar and concrete replacing cement. The addition of such a pozzolan reduces shrinkage as shown by laboratory experiments and through practice.

The generated data revealed very promising areas for further research in the field of HVFA high performance cements and concretes with significantly improved environmental profile enabling 46 % savings in energy and at least 40 % less CO_2 emissions.

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