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High Performance Concretes with Energetically Modified Cement (EMC)

# HIGH PERFORMANCE CONCRETES WITH ENERGETICALLY MODIFIED CEMENT (EMC)<sup>1</sup>

Lennart Elfgren, Jan-Erik Jonasson and Vladimir Ronin Luleå University of Technology, Sweden

#### SUMMARY

The demands of the modern building industry require development of new types of binder materials with improved properties for high and ultra high strength concretes and with significantly improved durability. They will provide new potential possibilities for the controlling of high performance concrete technology.

In the Department of Civil Engineering at Luleå University of Technology a study of energetically modified cement (EMC) indicates that it is possible to obtain much more rapid hardening cement than the original cement used. As an example the strength of EMC-concrete increases about 100 per cent at the age of one day compared with a conventional high strength concrete.

A new type of the cement gives possibilities to obtain required workability of the concrete mixtures with low water to binder ratios (w/B < 0.24) and achieve the strength levels up to 200 MPa with binder content not exceeding 550 kg/m<sup>3</sup>.

The modification process used in this study means a special mechanochemical treatment in vibrating milling equipment of the blend containing Ordinary Portland Cement (OPC) and silica fume (SF), which increases the surface energy and the chemical reactivity of the newly obtained binder. This results in an accelerating effect, which maintains at least for nine months.

According to ongoing investigations the energetically modified cement appears to give a considerable acceleration effect in the whole range of studied temperature. Concretes produced with EMC cement demonstrated very high durability at very severe testing conditions, including drying, saturation in sodium chloride solution and freezing-thawing. These results are very promising and it might be used in a lot of applications as winter concreting, precast element production, special structural elements, repair of buildings, rehabilitation, topping of concrete, floors, roads, etc.

### BACKGROUND

Energetically Modified Cement (EMC) is produced by high intensive grinding/activation of ordinary Portland cement (OPC) together with different types of fillers. Mechanical activation of mixtures containing different types of fillers involves the dispersion of solids and their plastic deformation. These processes cause the generation of defects in solids; they accelerate the

<sup>&</sup>lt;sup>1</sup> First published, M Schmidt, E Fehling & C Geisenhanslüke (eds), in: Proceedings International Symposium on Ultra-High Performance Concrete: Kassel, 13-15 Sept, 2004. Kassel University Press GmbH, pp. 93-102. Structural Materials and Engineering Series, vol. 3.

migration of defects in bulk, increase the number of contacts between particles, and renew the contacts. All these factors provide the chemical interaction between solids initiated by the highly efficient mechanical treatment that takes place in the milling devices, where impact and shear stresses are applied to the solid phase (planetary mills, vibrating mills, etc.). The following could be achieved by the milling process: (i) improved binding capacity of Portland cement fraction in combination with (ii) increased pozzolanic activity of fly ash, and/or (iii) improved chemical reactivity of blast furnace slag, and/or (iv) creation of hydraulic activity of recycled concrete due to opening of Portland cement unhydrated grains. The mentioned example is an illustration of nanostructuring of composite materials with use of special milling devices.

The EMC process was developed at Luleå University of Technology and at EMC Development AB, Sweden from 1994. Studies on the performance of EMC have been published by Ronin et al [1, 2, 3], Jonasson et al [4], Rao et al [5], Groth et al [6], Hedlund et al [7], Johansson et al [8], Elfgren et al [9], and Justnes et al [10-13].

This paper presents properties of high strength and ultra high strength cement pastes and concretes obtained by the use of energetically modified cements (EMC) developed in the department of Civil Engineering at Luleå University.

# **EXPERIMENTAL DETAILS**

In these experiments the main types of cement commercially produced in Sweden were used. They are ordinary Portland cement (Std P), rapid hardening Portland cement (SH P), and moderate heat liberating Portland cement (Std P Anl, or Anl for simplicity). Silica fume used in this investigation was produced by Elkem A/S in Norway and used as a pozzolanic additive. We used Mighty 100, a naphthalene type of superplasticizer, to the amount of 3 % of weight of the cement/binder in all the cement pastes and concrete mixtures.

EMC cements have been produced by intergrinding of the mentioned OPC and SF in a Humboldt Palla 20U vibrating mill. The blends of 2 kg material were subjected to milling for 30 min with porcelain cylindrical grinding media. EMC cements characterized by the fineness of 5500-6000  $\text{cm}^2/\text{ g}$  (Blaine).

All the types of cement mentioned above were subjected to energetically modification, and in this paper this treatment is referred to by abbreviation "EMC", which stands for Energetically Modified Cement, e. g. EMC(Std P) means the energetically modification of cement type Std P.

In these experiments the amount of silica fume was 5 to 20 % by weight of the cement. The water to binder ratio (w/B) for cement pastes was in the interval 0.16 to 0.20. All EMC pastes prepared for the strength tests had w/B equal to 0.16.

Concrete mixtures were produced with type Std P Anl both modified and non-modified. The cement content was 480 to  $550 \text{ kg/m}^3$ . Fine aggregate (0-8 mm) and coarse aggregate (12-16 mm) were used. The amount of silica fume (SF) was 10 to 20 %, and the amount of superplasticizer was 3 % by weight of the binder. The water to binder ratio (w/(C+SF) = w/B was from 0.19 to 0.27.

The cement pastes and concrete samples were cast at room temperatures (+20 °C) in 20x20x20 mm and 100x100x100 mm steel moulds, respectively. After casting the samples were put in

water. The cement paste samples were for compressive strength tested in an Dartec testing machine  $\pm 200$  kN,  $\pm 50$  mm, deformation rate 0.01 mm/s. The concrete samples were tested on the hydraulic testing press, SEGER 2000 kN.

The porosity of the cement pastes was examined with the use of mercury intrusion porosimeter Pore Size - 9310 (Micrometrics) with capacity of 30 000 psi. The samples were dried at 105  $^{\circ}$ C before testing.

The temperature effect on the hardening process was studied by measurements of strength growth at different hardening temperatures (5, 20, 35, and 50  $^{\circ}$ C, respectively). The test samples were cubes 100x100x100 mm stored in water.

The liberated heat at hydration of the concrete was calculated from measurements of the temperature development during adiabatic and semi-adiabatic conditions. Each test specimen was about four litres of concrete placed in a bucket of thin walled steel.

## RESULTS

### Strength of cement paste and concrete

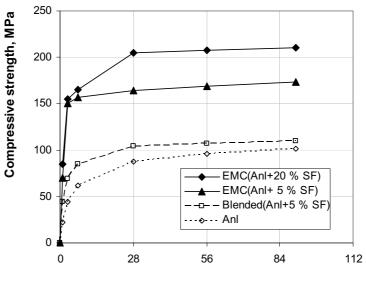
The results obtained show that the usage of EMC increases the strength of the cement paste hardened at +20 °C in comparison with non-modified cements, see table 1 for comparison of compressive 28 days strength and figure 1 for comparison of strength developments. This effect is especially profound at an early age (1, 3, and 7 days), where the value of the compressive strength of EMC pastes surpasses the strength of reference mixes in 1.8 - 2.0 times. This drastic rate of the strength was registered approximately at an equal level for all the types of cements used for both amounts of silica fume content. The main cause of this effect is probably the modification of the hydration products morphology, effective package of the calcium silicate hydrates and significant reduction of the cement paste porosity. An additional cause of this increase in this case is the reduction of w/B ratio from 0.18 to 0.16.

The use of EMC in concrete mix also significantly changes the rate of strength development. In this case for all levels of w/B ratios from 0.19 to 0.24, see figure 2, where very intensive hardening was observed in the early age - from 1 to 7 days. So, for an enough wide interval of water to binder ratio (from 0.19 to 0.24) and workability (slump from 7 to 110 mm), EMC can be an effective tool for high performance technology.

Table 1.	Compressive 28 days strength of cement paste for non-modified and EMC cements,
	respectively. Hardening temperature is about +20°C.

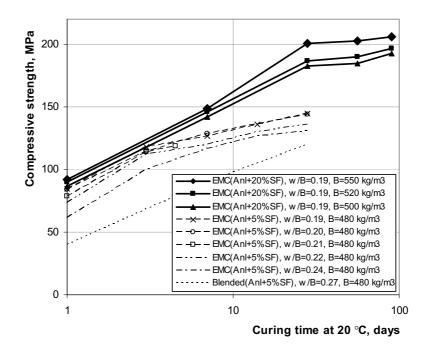
Amount of	Compressive strength (MPa) for					
silica fume by	Non-modified cement			Modified cement (EMC) based on		
per cent of cement weight	OPC	RHPC	Anl*	OPC	RHPC	Anl*
0	89.5	88.7	94.7	-	-	-
5	96.7	94.1	105.0	170.0	154.0	165.4
10	98.4	96.3	108.0	180.5	164.0	172.3
20	-	-	-	-	-	205.0

\*) "Anl" here means a moderate heat liberating Portland cement.



Curing time at 20 °C, days

**Fig 1.** Strength development at 20 °C curing for cement paste with water-to-binder ratio 0.16 with and without use of the EMC technology. "Anl" stands for a moderate heat liberating Portland cement.



**Fig 2.** Strength developments for EMC concrete mixtures with water to binder ratios from 0.19 to 0.24, and for concrete with non-modified cement at w/B equals 0.27. All samples cured in water at about 20 °C.

#### Structure of the cement paste

The mercury porosity results of cement paste samples with w/B = 0.2 cured at room temperature in water for 28 days are presented in figure 3. As can be seen in the figure, the introduction of

silica fume acted to refine the pore structure of the paste, and the usage of EMC shows an additional significant influence on the pore structure of the matrix. This influence is reflected in a decrease in total porosity as well as a decrease in the average diameter of the pores.

The examination of the EMC concrete fracture surface after strength testing of the samples showed an improved paste-aggregate bonding. The EMC concrete transition zone appears to be very dense without any visible microstructural gradients.

Properties mentioned above are expected to be favourable from the point of view of concrete durability. Long-term durability factors need to be studied to obtain EMC concrete performance parameters for durability design

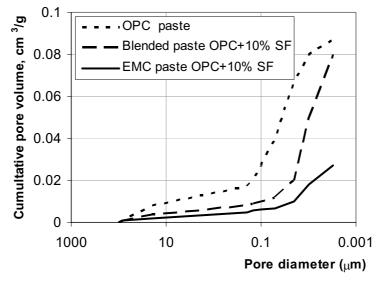


Fig 3. Pore size distribution

#### Maturity development

Measurements of strength growth at different temperatures for two types of concrete results in the relative maturity rates are shown in figure 4. The lower rate factor for the EMC concrete at temperatures above 20 °C is probably an effect of a reduction in the pore humilities due to self-desiccation.

As can be seen from figure 4, the scatter of the test data for each strength curve is rather small. This means that the concept of maturity rate only depending on the temperature works in a simplified model to take into account variable curing temperatures for early age concrete, see figure 5.

Resulting hydration heat for the two studied concretes is shown in figure 6, where it is obvious that the EMC concrete is significantly more rapid than the concrete made with non-modified cement.

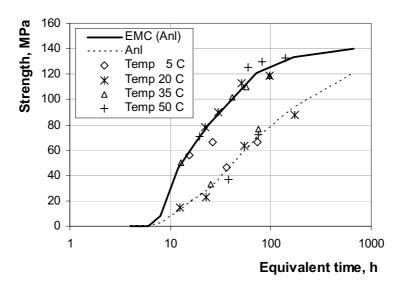


Fig 4. Compressive strength as a function of temperature-equivalent time

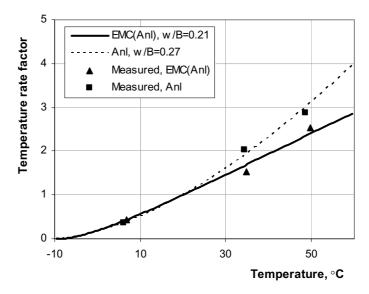


Fig 5. Temperature rate ratios as a function of time

One way to compare the hydration heat for these two concretes is to study the liberated heat per developed strength unit. This has been done by dividing the heat values from figure 6 with the strength values of figure 4. The result is presented in figure 7, where evidently the EMC concrete has a significantly lower heat production per strength unit than the concrete with non-modified cement. Furthermore, as the curve for the EMC concrete in figure 7 is almost horizontal it means that the liberated heat in this case is directly related to the strength growth for the whole range studied.

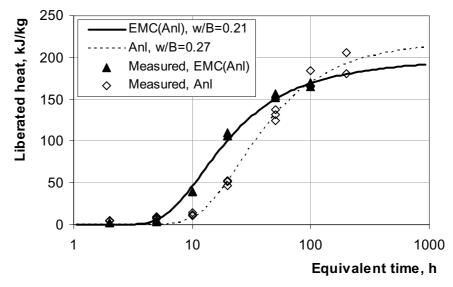


Fig 6. Liberated heat as a function temperature-equivalent time

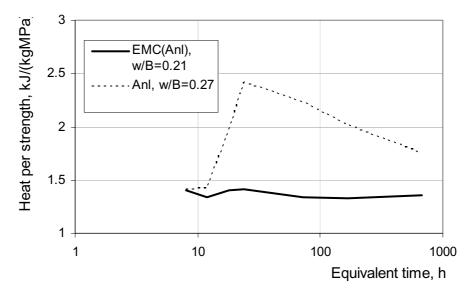


Fig 7. Liberated heat per strength unit as a function of temperature-equivalent time

#### **Durability**

Durability tests has been performed according to Bache [14], see scheme for one testing cycle in figure 8.

We should point out that this is one of the most severe testing procedures for concrete, which includes the sequence saturation by sodium chloride, drying and freezing. All steps mentioned in figure 8 are performed during 24 hours and is considered as 1 cycle.

EMC concrete and OPC concrete with, after 28 days of curing, compressive strengths 180.3 and 128.4 MPa, correspondingly, have been tested. Mass losses have been determined as a durability characterization.

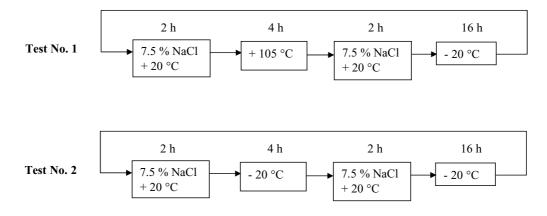


Fig 8. Test cycle scheme of durability tests.

EMC concrete showed rather high durability level during all testing period. Practically no scaling of the concrete has been observed. At the same time reference OPC concrete was totally destructed after about 16 cycles. This is in line with Bache's observations for high strength concrete with water-to-binder ration 0.25 subjected to similar testing procedure [14].

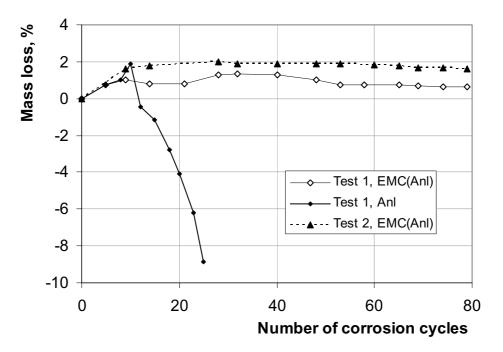


Fig 9. Mass loss of the concrete versus number of corrosion cycles

#### CONCLUSIONS

EMC cement has an important influence on the strength and structure of the hardened product:

- ultra high rate of strength development in wide range of curing temperatures
- higher absolute values of strength of the cement paste and concrete, which exceed 200 MPa
- EMC pastes have much lower porosity and more finer pore size distributions
- the liberated heat are rapid, but it is lower per strength unit compared with the use of nonmodified cement
- the amount of total liberated heat per cement weight for EMC concrete is approximately the same as for the concrete with non-modified cement
- EMC concrete demonstrated extremely high durability in very severe testing conditions

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Produced 2013-04

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EMC Cement B.V. Alvägen 33 SE - 97 332 Luleå Sweden

T/F: +46 920 89178 Cell/GSM: +46 705 498 892 E-mail: emcdev@telia.com

www.emccement.com

