The activation of pozzolanic materials with specific Cement Additives

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Introduction – the importance of pozzolanic materials in the modern cement production industry

In 2010 the worldwide cement production is estimated to have reached 3,3 billion tons [1] and is bound to maintain 2-digit growth numbers in the upcoming years. The cement industry is clearly taking its place in the new “world economy” scenario where political and physical borders are vanishing and internationalization is pushing companies to maximise efficiencies in order to be able to be competitive and guarantee the sustainability of the business. Cement manufacturers are showing enormous efforts in this field by trying to optimise the costs of clinker- and cement production and reduce CO_2 emissions to a minimum. New grinding systems like Vertical Roller Mills are playing an important role in this by reducing the specific energy consumption, but this is not enough to guarantee competitiveness and sustainability. During the past few years the cement industry is focusing more and more on the use of supplementary mineral additions. This is not a new approach, as norms allow the use of materials like limestone, slag, pozzolan and fly ash since decades, but the renewed interest in the optimisation of the use of those materials can be seen as “innovative” for the way in which it is interpreted today. In fact, the use of supplementary raw materials not only allows a reduction of costs (they are often much cheaper than clinker), but also creates an opportunity to reduce the specific CO_2 footprint of a cement. This article focuses on pozzolanic materials (natural pozzolan and fly ash) and the optimisation of the use of those materials with the help of specific Cement Additives.

The use of pozzolanic materials in cement

Cement producers are mainly using two types of pozzolanic materials:

- Natural pozzolan; most natural pozzolans are volcanic in origin, found usually in rock- or sand-like form. The usual active constituents are glass high in silica and often highly porous. Some pozzolans contain varying proportions of inactive materials as quartz, felspars, etc. Organic substances or clays can interfere with setting or strengths development [2].
- Silica Fly Ash (also called pulverized fuel ash) is separated from the flue gas of power stations burning pulverized coal. Chemical and phase compositions depend on those of coal and on the burning conditions. Amorphous (i.e. glassy) phases are the most reactive, while mullite and quartz are more inert [2].

The table below show the X-ray fluorescence analysis of two samples of natural pozzolan (Pozzolan I from Africa and Pozzolan II from Italy) and two samples of Fly Ash from Indian sources:

XRF	Pozzolan I (%)	Pozzolan II (%)	Fly Ash I (%)	Fly Ash II (%)
Al_2O_3	16,44	18,64	29,74	27,93
SiO_2	60,87	45,42	55,28	46,76
CaO	6,68	12,57	5,46	3,41
MgO	2,92	4,43	1,52	1,75
Na_2O	4,14	0,82	0,62	1,56
SO_3	0,09	0,03	0,26	1,42
Fe_2O_3	6,68	9,78	3,55	9,99
TiO_2	0,66	0,41	1,75	0,68
K_2O	1,13	5,70	0,80	4,12
Total	**99,61**	**97,80**	**98,98**	**97,62**

Table 1: x-ray fluorescence analysis of the pozzolan and fly ash samples

It is clear that there are fundamental differences between the different samples and above all between the two types of material. This means that the cement producers not only have to adapt their processes and parameters according to the characteristics of each type of material, but for every source of Pozzolan or Fly Ash (especially the amount of amorphous- and crystalline phases has to be considered), just as with other supplementary raw materials like Blast Furnace Slag [3].

The use of specific Cement Additives for the activation of pozzolanic cements

As mentioned before, the advantages of the use of pozzolanic materials in the cement recipe are mainly explained in terms of costs and the reduction of the specific CO_2 footprint of the cement, whereas the disadvantages are found mainly in the cement performance, because the above-mentioned materials often affect negatively (early) compressive strengths in comparison with cements with a high clinker content like OPC or CEM I. Moreover, as the previous analysis is showing, the extremely variable characteristics of the pozzolanic materials themselves cause significant variations in the effects they have when they are added to the cement. The use of specific and robust Cement Additives allows a significant improvement of the clinker / pozzolanic material ratio by activating the hydraulic phases of pozzolan and/or fly ash and therewith reduce the performance-gap with other cement types. For this purpose Mapei developed a new family of Pozzolanic Material Activators (hereafter simply called PMA's), containing particularly powerful performance enhancing compounds.

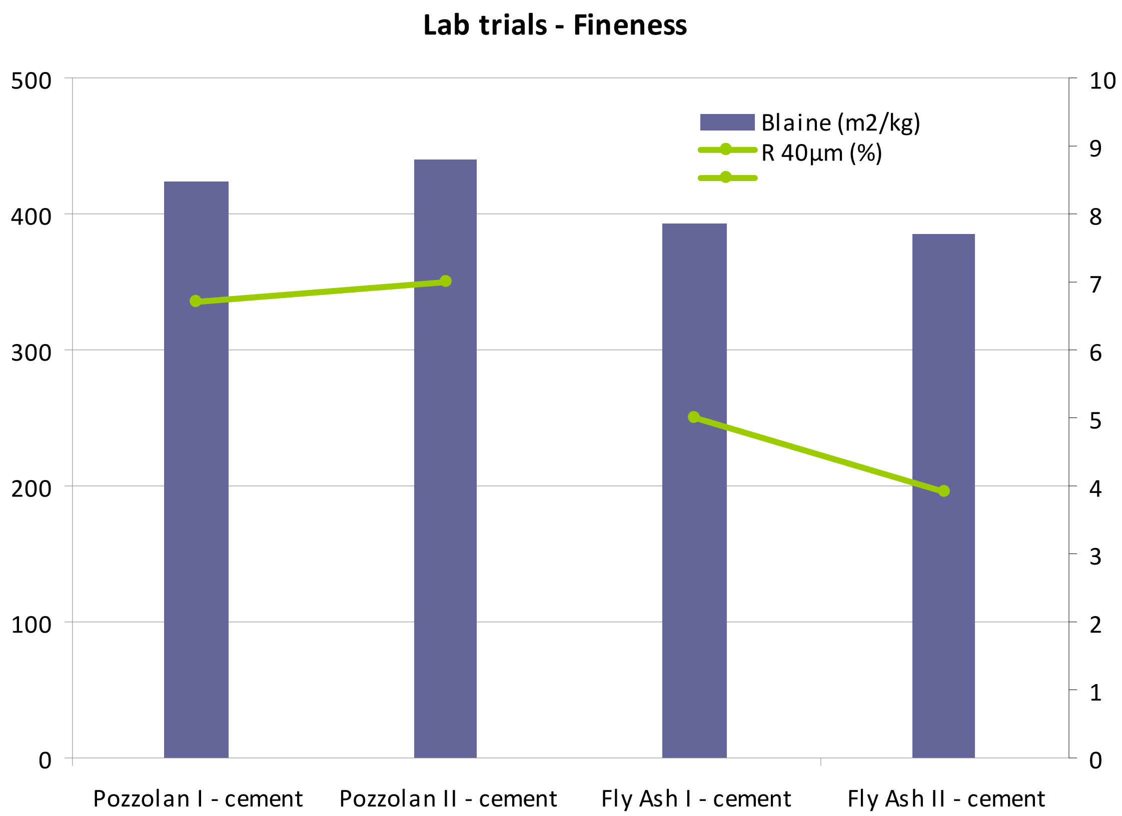
In this particular case we studied the effect of two types of chloride-free PMA's on cements containing natural Pozzolan or Fly Ash:

- PMA / LD; a specific low-dosage Cement Additive (dosage range between 300 and 500 g/t);
- PMA / HD; a specific high-dosage Cement Additive (dosage rate between 800 and 1.200 g/t).

Both additives were first tested on laboratory scale and afterwards during an industrial trial.

Laboratory-scale research

The laboratory-scale trials, performed in the MAPEI Central R&D facilities in Milan, Italy, were performed according the UNI-EN 196 standards, using standard clinker/gypsum and a Pozzolan or Fly Ash addition of 26%. The cements were ground in a laboratory-scale ball mill at standard time (i.e. same energy input), thus obtaining different fineness values because of the different mineral additions:



Graph 1: laboratory trials, Pozzolan- and Fly Ash-based cements - fineness

	Pozzolan I - cement	Pozzolan II - cement	Fly Ash I - cement	Fly Ash II - cement
Blaine (m^2/kg)	423	440	392	386
$R_{40\mu m}$	6,7	7,0	5,0	3,9

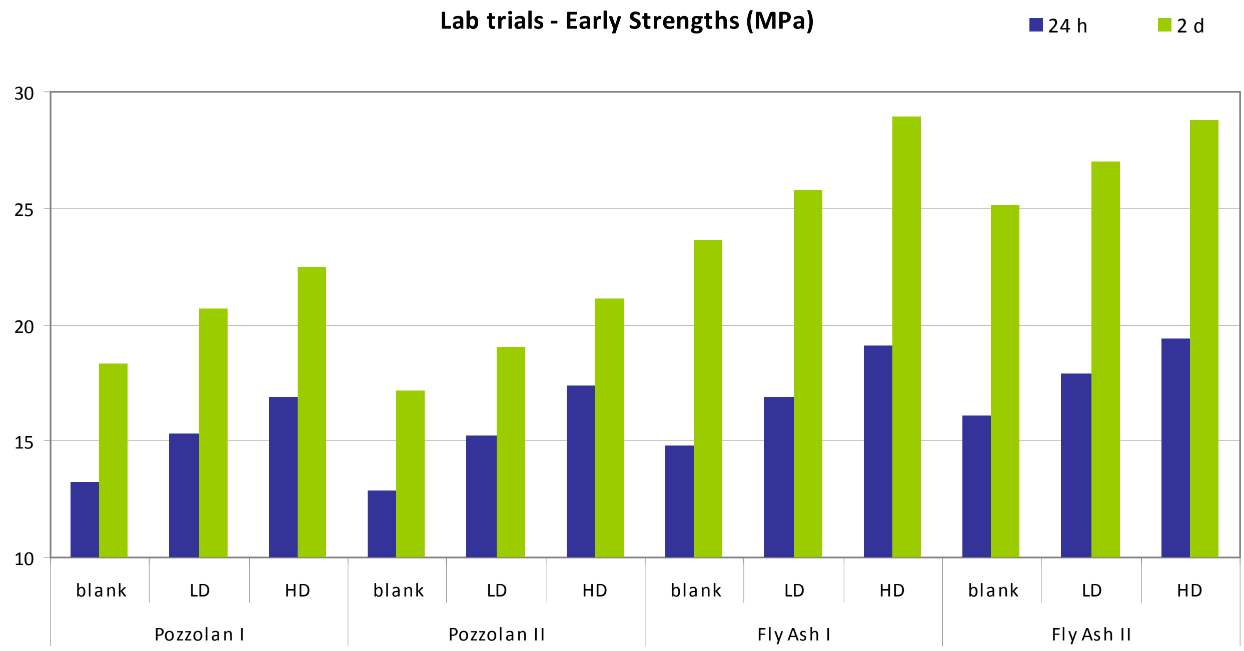
Table 2: laboratory trials, Pozzolan- and Fly Ash-based cements - fineness

With these cement samples we prepared standard mortars in order to study the strength development of each sample. This gave some interesting data about the performance of Pozzolan- and Fly Ash-based cement samples. The first thing we observed was the different behaviour of each sample of Pozzolan or Fly Ash in a condition where no additives were added ("blank"). For example, the cement containing Fly Ash II shows a better early strength development in comparison with Fly Ash I, whereas the two Pozzolan-containing cement samples show overall lower early strengths. This confirms not only the difference between Pozzolans and Fly Ashes, but also the fact that no two Fly Ashes or Pozzolans are the same.

	Pozzolan I - cement			Pozzolan II - cement			Fly Ash I - cement			Fly Ash II - cement		
	blank	LD	HD	blank	LD	HD	blank	LD	HD	blank	LD	HD
24 h	13,2	15,3	16,9	12,9	15,2	17,4	14,8	16,9	19,1	16,1	17,9	19,4
2 d	18,3	20,7	22,5	17,2	19,0	21,1	23,6	25,8	28,9	25,1	27,0	28,8
28 d	33,7	36,1	37,6	32,5	35,7	36,9	41,0	43,6	46,2	42,3	44,9	47,3

Table 3: laboratory trials, Pozzolan- and Fly Ash-based cements – strengths (MPa)

The following graph shows in detail the comparison of the 24 hours- and 2 days strengths:



Graph 2: laboratory trials, Pozzolan- and Fly Ash-based cements – strengths (MPa)

When looking at the performance of the two PMA's, we saw a clear and constant effect on the early strength development. In all cases the high-dosage Cement Additive showed a more significant effect on the strengths if compared with the low-dosage product, whose performance was in any case interesting.

Industrial application

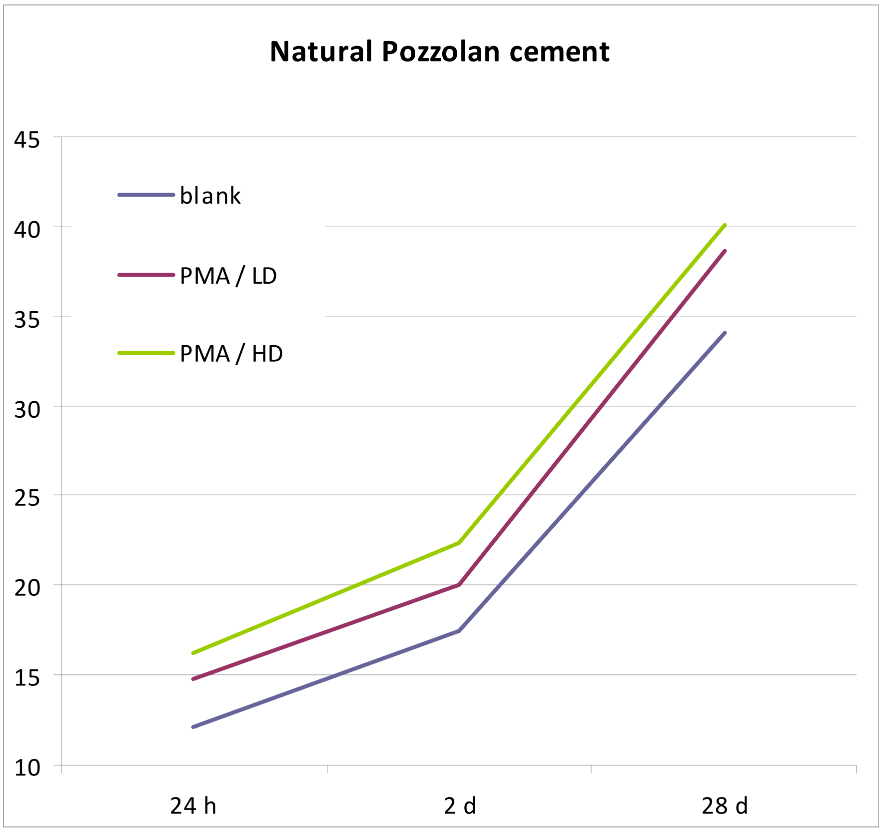
After the laboratory-scale evaluations, both Cement Additives were tested industrially during a two-week period in Africa (in this case an addition of Natural Pozzolan of 30%) and India (26% Fly Ash):

	Africa	**India**
Grinding system	Traditional Ball Mill	Vertical Roller Mill
Make	F.L. Smidth	Loesche
Pozzolan addition (%)	30	-
Fly Ash Addition (%)	-	26
Cement Blaine fineness (m^2/kg)	380	340
Throughput (t/h)	110 – 125	225 – 245
PMA/LD dosage rate (g/t)	350	350
PMA/HD dosage rate (g/t)	1.000	1.000

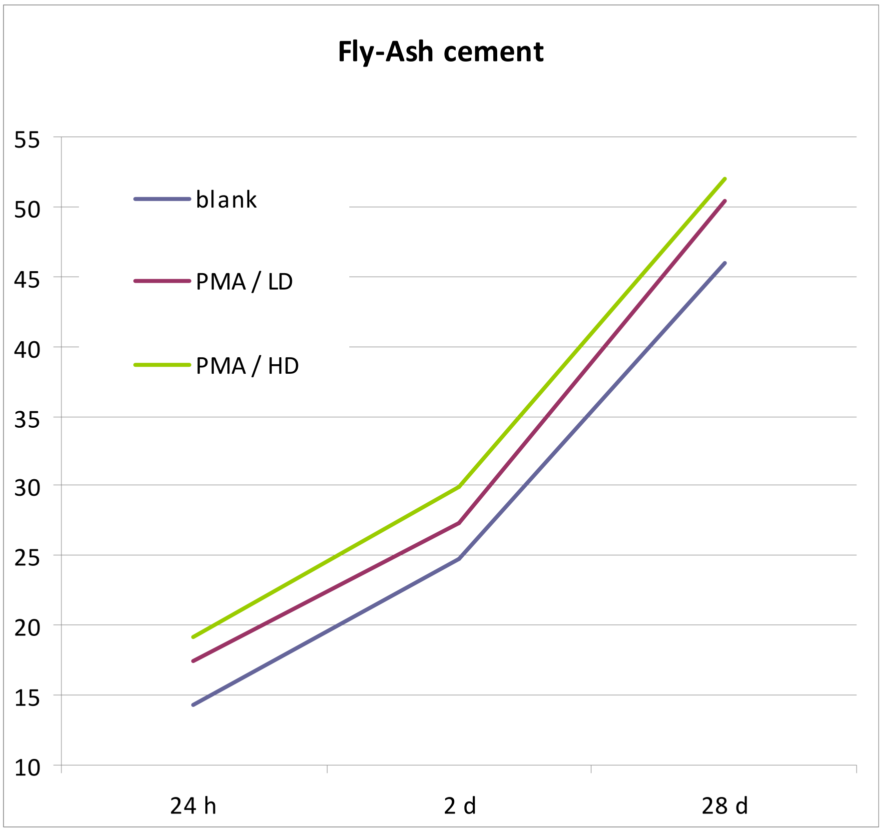
The fineness parameters were kept as constant as possible during the trial. The average results in terms of strength improvement are shown in the following table and in the graphs below.

	30% Pozzolan (Africa)			26% Fly Ash (India)		
	blank	LD	HD	blank	LD	HD
24 h	12,1	14,8	16,2	14,3	17,4	19,2
2 d	17,5	20,0	22,4	24,7	27,3	29,9
28 d	34,1	38,6	40,1	45,9	50,4	52,0

Table 4: industrial trials, Pozzolan- and Fly Ash-based cements – strengths (MPa)



Graph 3: industrial trials, Pozzolan-based cement – strengths (MPa)



Graph 4: industrial trials, Fly Ash-based cement – strengths (MPa)

From these industrial tests we can conclude that the laboratory results can be confirmed in an industrial application as well. Moreover, we can clearly see that the PMA/HD shows a better performance in both cases, most probably because of the higher content of Performance Enhancing components.

Conclusion

By using specific and highly sophisticated Cement Additives it is possible to maximise the pozzolanic material addition in cements, therewith improving cost efficiencies and reducing the specific CO_2 footprint. Our practical experience in different countries and with different grinding systems shows that the PMA products are robust and well performing in various situations. In a worldwide scenario where enormous amounts of cement are produced, the further optimisation of the use of supplementary raw materials can lead to huge savings in terms of costs and CO_2 emissions, thus generating vast opportunities for the business to create long-term growth in a competitive and sustainable setting.

Bibliography

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