Cement Additives Division

Cement Additives as performance enhancers for Portland pozzolanic cements

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Abstract

The use of natural pozzolans as cementitious materials dates back to the birth of the first building industry, more than 2000 years ago. In modern cements, pozzolans still maintain their importance due to the possibility of clinker reduction. On the other hand, the use of pozzolanic materials as a clinker substitution in Portland cements leads to performances modifications, usually related to early strengths decrease and increase of water demand with subsequent slump loss. After a short introduction about the history of natural and artificial pozzolans and about their chemical and physical characterization, in this paper we focus on the use of chemical additives to overcome any modifications of cement performances at high pozzolan content.

Introduction

In 2011 global cement production worldwide has been reported to be close to 3.6 billion tons, with China accounting for about 57% of the total. Asia and Africa cement production growth rate, although lower than expected, has been showing positive increase, while Europe and North America suffered due to the economic downturn [1]. Cement production is reported to contribute about 5% to global anthropogenic carbon dioxide emissions [2], mainly related to clinker production (due to decarbonation of limestone and the use of fossil fuels in order to reach the elevated temperatures needed for clinkerisation process).

The use of pozzolans (that dates back to more than 2700 years ago) in building industry has gained a remarkable importance, both for lime/pozzolan mortars and for pozzolan based cements. In the last years, the general tendency of the global industry towards greenhouse gases reduction has forced the cement manufacturers to find mineral additions in order to reduce the clinker content. Together with fillers such as limestone (that do not give a remarkable contribution to compressive strengths), secondary cementitious materials with partial hydraulic properties (thus partially contributing to strengths, especially at late ages) are widely used. Blended cements, in which part of the clinker is replaced by industrial or natural by-products, such as blast furnace slag, coal fly ash, natural volcanic pozzolan, limestone, play a key role in reduction of greenhouse gases emissions.

According to standard definition, pozzolan is a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious properties but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties. This chemical reaction between the siliceous/aluminous components, calcium hydroxide and water is called the pozzolanic reaction.

In this paper we describe in details the use of pozzolan in cement, with particular reference to the optimization of pozzolan cement properties with the addition of chemical cement additives.

History of pozzolan cements

In the Greek island of Santorini (that surrounds a lagoon formed after a volcano eruption of in 1600 BC, probably one of the largest volcanic events on Earth in recorded history) natural pulverulent materials were mixed with lime and used as mortar for constructions in contact with water. This is probably the first documented use of natural pozzolans in building applications.

Figure 1 - “Pont du Gard” aqueduct, built in France during the 1st century with lime/pozzolan mortars.

The Roman writer, architect and engineer Vitruvius, in his fundamental opera “De architectura” (1st century BC), widely described the use of natural pozzolans, very common in central-southern Italy. Actually, the name pozzolan is derived from latin “*pulvis puteolanus*” that means “powder from Pozzuoli”, a city near Naples (central Italy). Vitruvius reported several recipes for mortars (two parts pozzolan, one part lime) and concrete (pozzolan, lime and stones) to be used for undersea constructions. Using this technology, several bridges, harbors, aqueducts and temples were built and most of them are still in use. Samples of these ancient constructions were tested for compressive strengths and reached values close to 5 MPa: quite high, considering that the mortar have been subjected to the action of sea water for about 2000 years [3].

After the invention of Portland cement (first half of 1800), the use of pozzolan as concrete ingredient and as mineral addition in blended cements started. At the beginning of 1900 Bruno and Bougleux in Italy [4], Michaelis in Germany [5] and Ferét [6] in France proposed blends of cement and pozzolan for the manufacturing of concrete to be posed under sea water, with the requirement of high specific surface of pozzolan in order to increase the reactivity. High durability properties of pozzolan cements lead to the definition of specific standards, such as ASTM C618, ASTM C311 and EN 197-1, for pozzolan cements.

Figure 2 - Pantheon, built in Rome during the 2nd century. The perfect semi-circular rotunda was realized with lime/pozzolan concrete with different density from bottom to the top, in order to reduce tensile stresses.

Nowadays, the wide availability of natural pozzolan in several areas and the needs for greenhouse gas emission reduction has given new importance to pozzolan cements.

Characteristics and chemical/physical characterization of pozzolans

The history of pozzolan use is not merely a curiosity, but clearly indicates the main features of this material:

- Volcanic origin: the hydraulic activity of pozzolans is related to the presence of silicon and aluminium and to the amorphous structure. Such highly porous glassy materials are usually formed in volcanic areas due to geological modifications. Crystalline part of pozzolan usually contribute less or not at all to the reaction with lime. It is well known that most common natural pozzolans are of volcanic origin: trass, certain pumicites and perlite. Man made pozzolans also exist. These are materials rich of silicon obtained as by product of other industrial processes. Typical examples are blast furnace slag from steel industry, fly ashes from coal and oil combustion power plant, silica fume from silicon manufacture.

- Pozzolanic reaction: natural pozzolans in themselves do not possess cementitious properties. The use in building applications is based on the reaction with calcium hydroxide. The latter must be supplied, usually in form of lime (as it happened in Roman concrete) or in form of portlandite (calcium hydroxide) formed during clinker hydration, in modern pozzolan cements.

- High durability: lower calcium hydroxide in hydrated pozzolan cement pastes (due to further reaction of calcium hydroxide with silicon/aluminium contained in pozzolans) reduces the possibility of attack from sulfate and sea water. Magnesium chloride contained in sea water promotes the conversion of calcium hydroxide to calcium chloride and magnesium hydroxide (that expands during precipitation, thus damaging concrete structure), according to the following reaction:

$$Ca(OH)_2 + MgCl_2 = CaCl_2 + Mg(OH)_2$$

  If calcium hydroxide in cement pastes is reduced, damages due to magnesium hydroxide precipitation are limited. In addition, in modern pozzolanic cements the lower hydration heat is highly appreciated for massive constructions, where heat dispersion can be critical.

Typical chemical composition range of natural pozzolans is summarized in the table.

Loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Alcali
3-8%	45-65%	15-25%	3-12%	2-12%	0-4%	0-2%	4-12%

Problems related to the use of pozzolans

Although allowing several advantages, the introduction of pozzolan in Portland cement manufacturing (and consequently the reduction of clinker) leads to some performances modifications that need to be overcome.

1. Strengths: hydraulic activity of pozzolans requires the presence of calcium hydroxide. As a consequence, the strength contribution of pozzolanic materials can be noticed on late strengths, when high amounts of calcium hydroxide are available from C_3S reaction. At early ages the reduction of clinker leads to a general decrease of compressive strengths.

2. Slump decrease and increased water demand: the high fineness of amorfous pozzolan and sometimes its porosity increase the water demand of cements. As a consequence, with the increase in natural pozzolan content, the cement mortar flow or concrete slump generally is reduced.

3. Grinding: general behavior of natural pozzolan during cement grinding is characterized by its water content, softness (in comparison to clinker) and tendency to coating on grinding media and mill lining. This usually poses some problems during grinding.

Figure 3 shows the effect on compressive mechanical strengths when clinker content is substituted with pozzolan. Data refers to a lab testing with the following procedure [7]:

- Reproduction of an OPC by grinding in lab ball mill (95% clinker with 5% gypsum, Blaine specific surface 4700 cm2/g).

- Grinding of pozzolan at 10±1% residual material through a 32 µm air jet sieve.

- Blending of OPC and pozzolan in different proportions.

- Determination of mortar compressive strengths according to European standard EN 196-1.

In the graph, the strengths percent decrease with reference to the initial OPC (0% pozzolan content) is reported in function of pozzolan content. Results clearly show that the early strengths rapidly decrease even at low pozzolan content, while at later ages higher substitutions (10-15%) are possible without any particular difference. This is due to hydraulic properties of pozzolan, that develop on the long run secondary C-S-H that substitute the clinker hydration products.

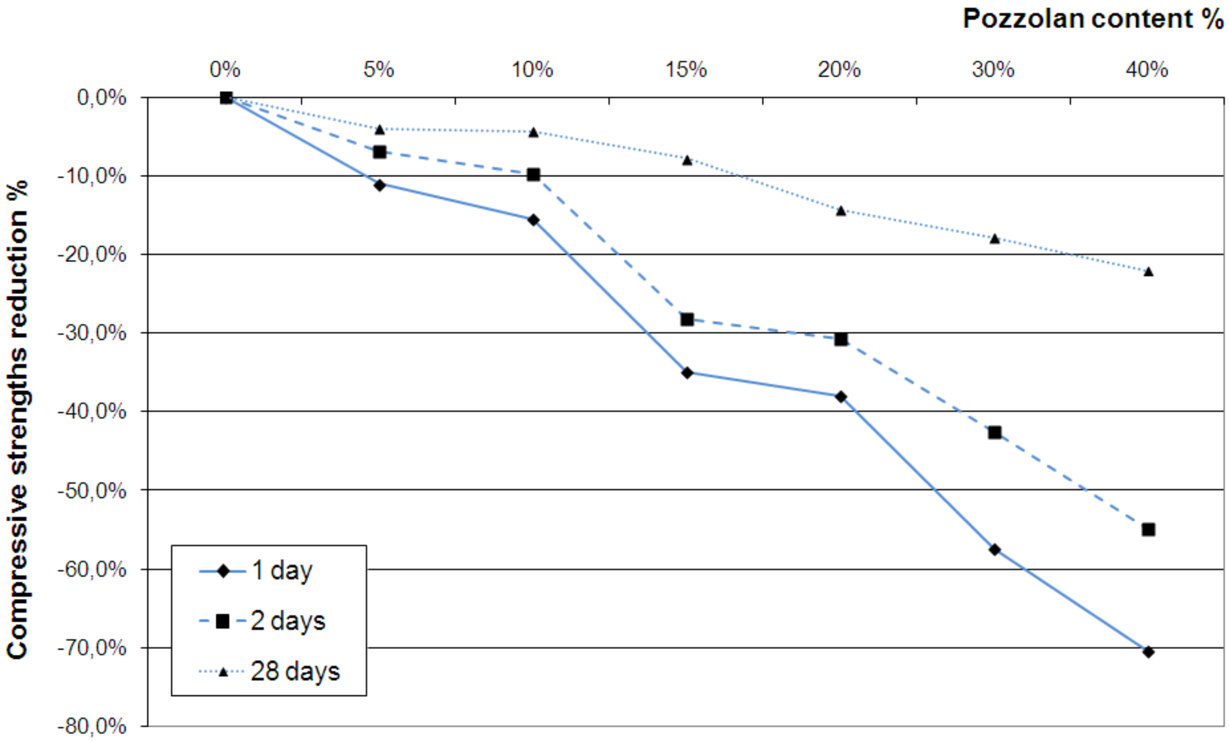

Figure 3 - Effect of pozzolan content on mortar compressive strengths.

It is interesting to compare the effects of clinker substitution with different mineral additions: limestone (considered an inert filler), blast furnace slag (typical example of artificial pozzolan material) and natural pozzolan. Figure 4 summarizes the 28 days mortar compressive strengths decrease when clinker is substituted with the above mentioned mineral additions. Slag has the best performances: substitutions up to 20% are possible without particular decrease of strengths. Pozzolan is less performing than slag, but definitely more than limestone, which promotes a steep drop in late strengths. This different behavior is well recognized in international standards. For example, European Standard EN 197-1 on cement compositions allows the use of slag up to 95% (type CEM III/C), pozzolan up to 55% (type CEM IV/B) but only maximum 35% limestone (type CEM II/B-L).

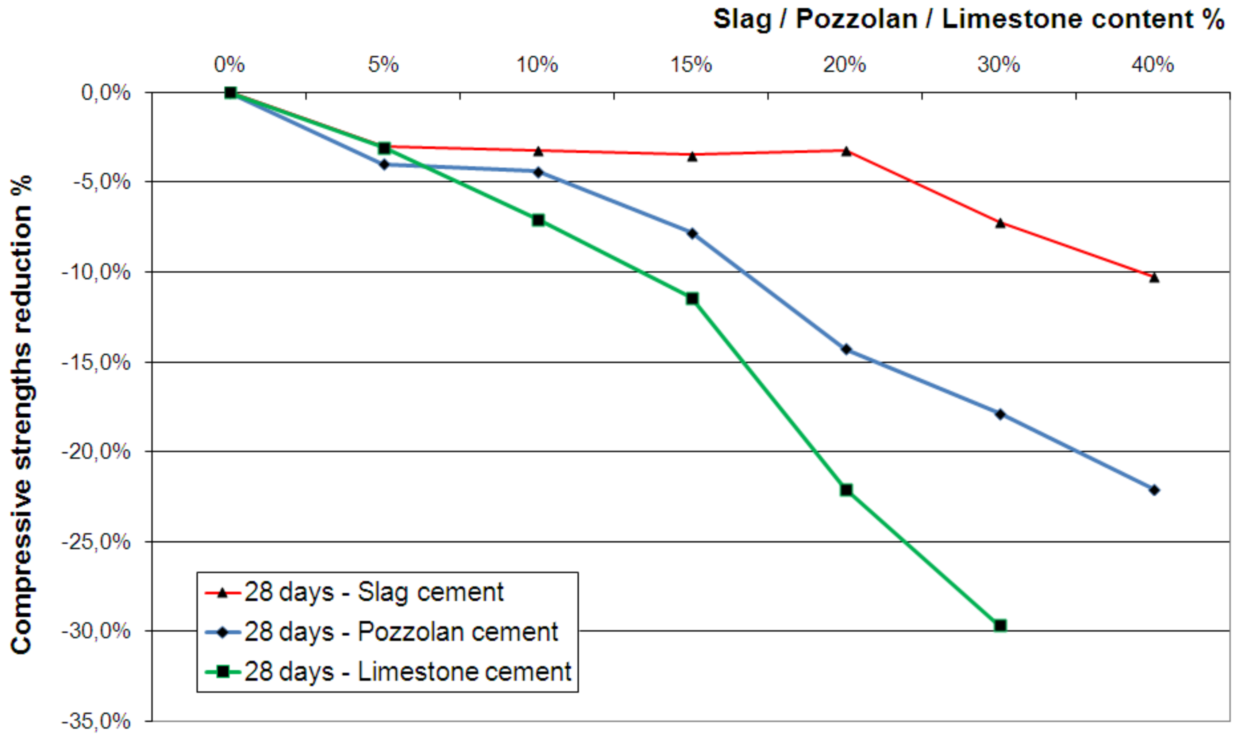

Figure 4 - Effect of different additions on 28 days mortar compressive strengths.

There is also a very evident difference between slag and pozzolan when water demand of blended cements is compared. Figure 5 reports the mortar workability (flow, thus the measurement of the ability of a mortar to spread over a surface - several test method such as ASTM C1437 or EN 1015 are available). It can be seen that the use of pozzolan may promote a decrease in workability, due to an increase in water demand related to high porosity of natural pozzolan. On the other hand, blast furnace slag addition (that does not have a porous structure) allows improvement in workability. This is related to the fact that more water is available due to clinker reduction.

The use of cement additives on pozzolanic cements and related case studies

Considering the effect of mineral addition increase on cement performances described in the previous paragraph, it follows that the possibility of higher clinker substitution is directly related to the possibility of maintaining acceptable strengths values. One of the most promising technologies for pozzolan cements production is related to the use of grinding aids.

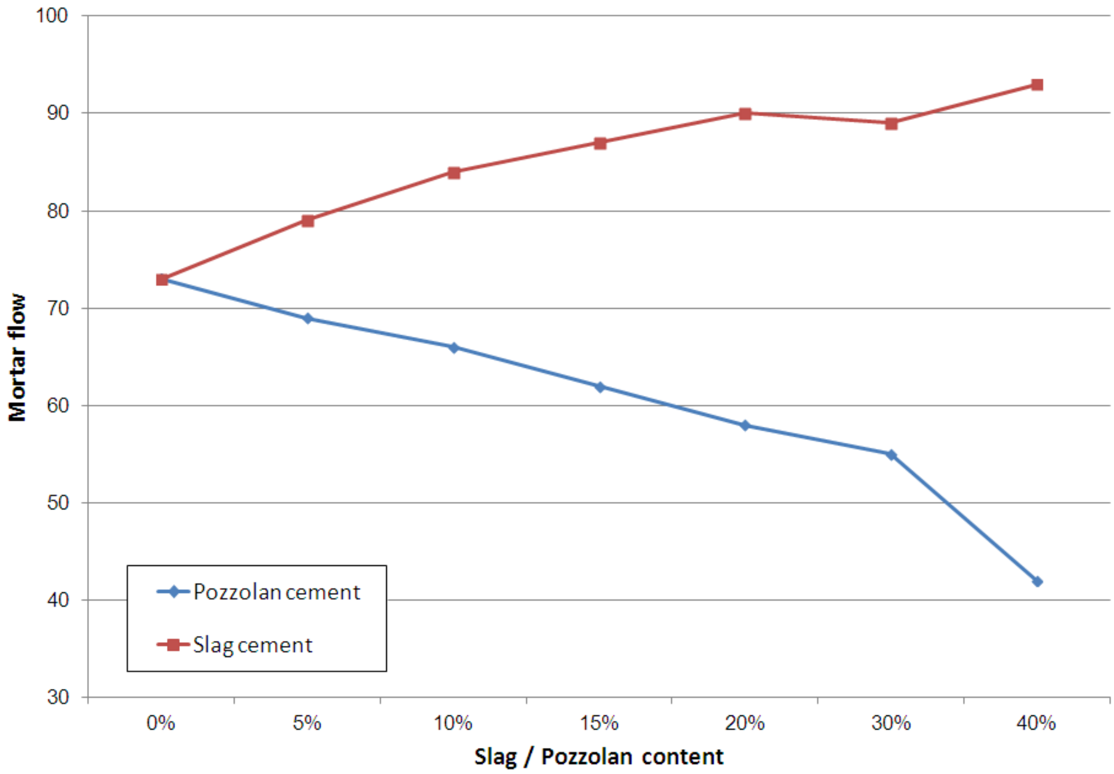

Figure 5 - Effect of different mineral additions on mortar workability.

Cement grinding aids are process additives used during finish grinding in order to reduce cement pack set inside the mill and to increase production. Grinding aids act by coating the particles which cause agglomeration with a mono-molecular layer which neutralizes the surface electrical charges. This reduces significantly the energy needed to grind, allowing interesting reduction of the specific consumption (in terms of kWh/t) [8]. In the last years, cement grinding aids have faced an evolution, and nowadays we usually consider the use of performance enhancers: these can be viewed as products not only reducing the energy needed for cement grinding, but also improving the performances of cements, in terms of compressive strengths and workability. These products allow the cement producer to reduce the amount of clinker in the cement recipe, thus minimizing the environmental impact as well as saving energy and fuel.

Generally speaking, the main parameters that affect reactivity of natural pozzolans are the following:

- Rate of calcium hydroxide (portlandite) production during tricalcium silicate hydration. Pozzolans are substantially low in calcium, thus formation of C-S-H proceeds only when calcium is supplied in form of $Ca(OH)_2$ during clinker hydration. The faster is the supply of calcium, the higher is the reaction degree of pozzolan.

- Rate of dissolution of mineral addition: the faster the pozzolan supplies silicon or aluminium to the pore water, the faster is the formation of secondary C-S-H. Dissolution rate is related to the pH of pore water, to the particle size distribution of addition and to the presence of chemicals that can promote the dissolution.

A grinding aid intended to be used for improvement of pozzolan cements performances should be designed and formulated in order to be active as accelerator of clinker hydration, allowing higher amounts of calcium hydroxide to be available for secondary materials activation. In addition, thanks to the reduction of cement pack-set during grinding and consequently to the reduction of energy required, higher fineness and better particle size distributions are possible, thus improving the dissolution rate of mineral additions. The following case studies better clarify the benefits given by grinding aids.

Case study 1 - Clinker reduction in pozzolan cement

High clinker substitutions are always associated to a drop in compressive strengths. In order to overcome this, a suitable grinding aid should be used. A cement (20% pozzolan) was tested for possibility of increasing pozzolan to 25%. During a long industrial trial, the use of a specific performance enhancer was evaluated. Results are summarized in the following table.

	Cement 1	Cement 2	Cement 3
Clinker %	75	70	70
Gypsum %	5	5	5
Pozzolan %	20	25	25
Additive (g/t) MA.G.A./C115	-	-	450
Residual 45 µm (%)	15	16	12
24 h mortar strengths	17.3	14.2	17.1
28 days mortar strengths	43.5	41.6	44.3

The use of MA.G.A./C115 allowed the increase of early and late strengths thus producing a cement with 25% pozzolan content, but with the same performances as higher clinker cement.
These results can be explained considering both the chemical action on clinker hydration (acceleration of calcium hydroxide production) and the improvement in particle size distribution.

Case study 2 - Performances improvement on a CEM IV/B-P 32.5 R type cement

An industrial evaluation of the grinding additive MA.P.E./W 1111, a liquid product for the production of pozzolanic cements specifically formulated with raw materials of the highest quality, was performed during production of a CEM IV/B-P 32.5 R cement (40% pozzolan content). The trial consisted in grinding a cement at the same level of fineness, with and without the addition of MA.P.E./W 1111, verifying immediately the effects on mill productivity and successively on workability, mechanical strengths and separation performance. Results of the tests are summarized in the table below.

Details	Blank	MA.P.E./W1111
Cement	CEM IV/B-P 32.5 R	CEM IV/B-P 32. 5 R
Additive dosage (g/t)	---	2.700

Production (t/h)	83,9	93,8
Passing material at 40 µm sieve (%)	80	81,5
Workability (flow)	36	48
Mortar strengths at 24 hours (MPa)	8,0	10,6
Mortar strengths at 2 days (MPa)	16,3	18,5
Mortar strengths at 28 days (MPa)	34,9	40,3

The results obtained from the industrial trial have confirmed the triple action of the additive MA.P.E./W 1111 and continuous utilisation of this product gives the following benefits:

- Increases in productivity.
- Cement mechanical strength increases.
- An increase in the workability of the cement. The inferior water demand reduces the consumption of cement and helps the synergy with plasticizer additives employed in the production of concrete.

A detailed description of this industrial experience is available elsewhere [9].

Conclusions

After more than 2000 years, the building industry still relies on the use of natural pozzolans. Despite the advantages of clinker reduction (and greenhouse gases emission cut), high durability and low hydration heat, performances of pozzolan cements can be affected in terms of lower strengths and workability. The use of grinding aids in pozzolan cements production represents probably the easiest way to improve the performances of blended cements. The effect of grinding aids is related to amelioration of fineness and particle size distribution and to the accelerated clinker hydration, allowing higher amounts of calcium hydroxide to be available for activation of mineral additions and consequently for higher mechanical properties.

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