Clinker savings using additives

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The reduction of carbon dioxide release associated with decarbonation of limestone and with the use of fossil fuels is probably the main issue the European cement industry will have to face in the coming years. For each tonne of clinker coming out of the kiln, approximately 800kg of greenhouse gases are produced. It has been reported that cement production accounts for about five per cent of total CO_2 of anthropoganic origin[1].

To reduce the emissions of greenhouse gases the production of blended cements (where the clinker is reduced by adding alternative material with hydraulic properties) is strongly increasing. The use of blast furnace slag, pulverised fuel ash, limestone or pozzolana as a constituent of cements reduces the clinker requirement and this lowers the CO_2 emissions[2].

Blended cements present interesting advantages (such as lower heat of hydration, higher durability and resistance to chemical attack), but the performances are usually lower than ordinary Portland cements. The innovation consists in finding new technologies allowing the use of alternative materials while keeping unaltered the cement performances.

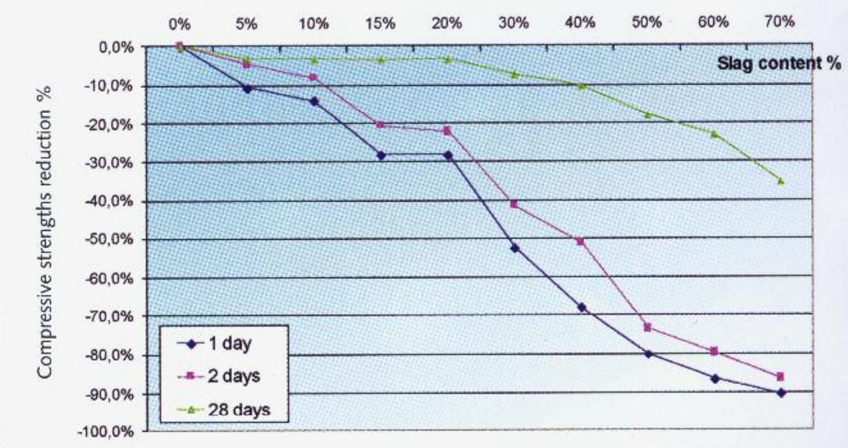

Figure 1: compressive strengths reduction vs slag content

Blast furnace slag cements

Blast furnace slag is formed as a liquid in the manufacture of iron. If rapidly cooled, it forms a glass with latent hydraulic properties. The glass content, fineness and composition (particularly the amount of SiO_2, Al_2O_3, CaO and MgO) are the basic parameters that control the reactivity of the slag[3].

The use of slag (and other pozzolanic materials) as mineral additions to cements is based on its latent hydraulic properties: when mixed with clinker, the calcium hydroxide supplied from alite hydration is used by silica and alumina contained in slag to form calcium silicate and calcium aluminate hydrates, thus contributing to strength development.

The principal hydration products and the microstructure are essentially similar to those given by pure Portland cements, but the quantities of portlandite (calcium hydroxide) found in the hydrated pastes are lower, since this has been consumed by slag hydration[3].

A general discussion about the characteristics of blast furnace slag cements and the use of grinding aids has already been presented elsewhere[4]. In this article we will describe how the compressive strengths of slag cements are affected by clinker reduction. The aim is to present the results of a lab

Table 1: characteristics of clinker and gypsum

Clinker chemical composition (by X-ray fluorescence)	*(%)*	*Clinker mineralogical composition (by quantitative X-ray diffraction/ Rietveld method)*	*(%)*
Loss on Ignition	0.27	C_3S	69.2%
SiO_2	19.74	C_2S	8.7%
Al_2O_3	6.23	C_3A	17.1%
Fe_2O_3	2.52	C_4AF	2.1%
CaO	66.45		
MgO	1.36		
SO_3	1.50		
Free CaO	1.10		
Gypsum composition (by quantitative X-ray diffraction/Rietveld method) (%)			
Gypsum ($CaSO_4 \cdot 2H_2O$)	80		
Anhydrite ($CaSO_4$)	15		
Calcium carbonate ($CaCO_3$)	5		

Table 2: characteristics of slag samples

Chemical composition (by X-ray fluorescence)	*Slag 1 (%)*	*Slag 2 (%)*	*Slag 3 (%)*	*Slag 4 (%)*
SiO_2	37.67	35.28	38.68	38.11
Al_2O_3	5.89	10.63	7.35	8.15
Fe_2O_3	1.61	0.89	0.79	1.10
CaO	43.79	40.73	41.27	45.14
MgO	5.61	6.49	8.13	5.12
Mn_3O_4	1.12	1.10	0.98	1.15
$(CaO + MgO + Al_2O_3)/SiO_2$	1.47	1.64	1.47	1.53
Glass content (by X-ray diffraction/Rietveld method, internal standard: rutile) (%)	97.7	95	100	96%

Table 3: cements composition

Cement sample	*Clinker (%)*	*Gypsum (%)*	*Slag (%)*	*Cement type according to EN197-1*
1	95.0	5.0	0	CEM I
2	90.3	4.7	5	CEM II/A-S
3	85.5	4.5	10	CEM II/A-S
4	80.8	4.2	15	CEM II/A-S
5	76.0	4.0	20	CEM II/A-S
6	66.5	3.5	30	CEM II/B-S
7	57.0	3.0	40	CEM III/A
8	47.5	2.5	50	CEM III/A
9	38.0	2.0	60	CEM III/A
10	28.5	1.5	70	CEM III/B

investigation describing in practice the effect of chemical additives on cement performances, giving some practical advice for slag cement optimisation.

Effects of slag content increase on compressive strengths

Several slag cements have been reproduced in our lab by grinding clinker and gypsum and blending the resulting CEM I with four different types of ground slag. The fineness of CEM I (expressed in terms of Blaine specific surface) has been kept constant at 4700cm2/g, and the slag has been ground to 10.0±1.0 per cent passing material through a 32μm air jet sieve.

The characteristics of clinker and gypsum are reported in Table 1, while Table 2 reports the composition and glass content of the four slag samples used.

In Table 3 the cements reproduced and their compositions are summarised.

For each cement, mortar compressive strengths at 1, 2 and 28 days have been evaluated according to European Standard EN 196-1 and the results averaged between the four slag types. It is interesting to point out that the fineness of cement and slag and the ratio between clinker and gypsum are always the same. This means that the differences in compressive strengths are related only to slag content.

The effect of slag content increase on the compressive strengths at 1, 2 and 28 days is reported in Figure 1. The data is expressed as a percentage reduction in comparison to pure Portland cement. For example, after replacing five per cent of clinker with slag there is a 10 per cent reduction of one-day strength. The effect of hydraulic properties of slag can clearly be seen. At later ages the compressive strengths up to 20 per cent slag are quite similar to Portland cement and only if the slag exceed 30 per cent the decrease become more pronounced. The reason of this behaviour lies in the fact that the activation of slag requires the availability of portlandite: as the hydration proceeds, more calcium hydroxide is released by clinker and the percentage of slag reacted increases, thus enhancing the contribution to compressive strengths. On the other hand, the negative effect of clinker reduction on early ages is evident. The decrease in performances is almost linear, as the slag content increases.

The use of performance enhancers in slag cements

A good way for limiting the negative effect of clinker reduction on strength is the use of cement grinding aids. Beside the positive effect on grinding (increase in mill output and/or fineness) there is a positive influence on clinker reactivity. During hydration of silicate minerals (in particular tricalcium silicate) calcium hydroxide and

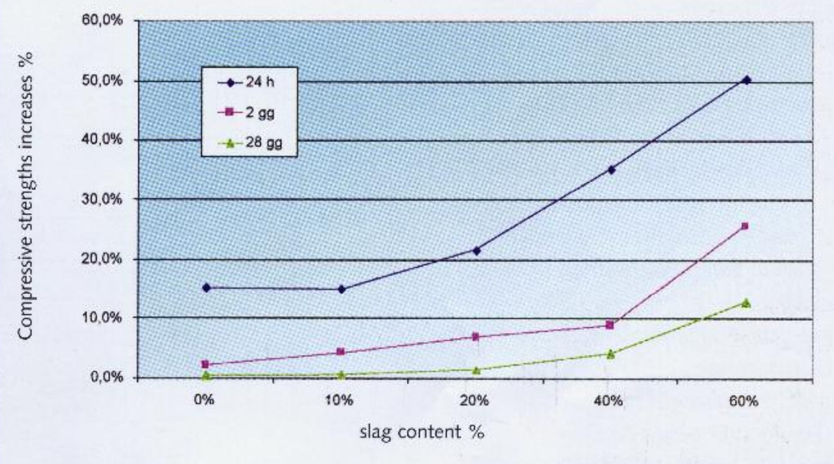

Figure 2: compressive strength increase with MA.P.E./S cement additive

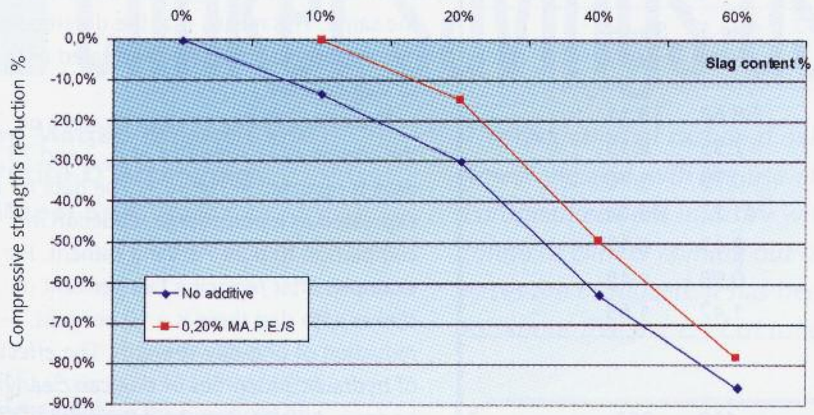

Figure 3: one-day compressive strength reduction vs slag content with and without MA.P.E./S

amorphous calcium silicate hydrates (C-S-H) are produced, the latter being the main responsible for compressive strengths development. If the degree of hydration is increased by the presence of the additive, more C-S-H and more calcium hydroxide are formed. Calcium hydroxide reacts with slag giving further C-S-H and the positive effect on strength is amplified.

Benefits from performance enhancers

Samples of cements with 10, 20, 40 and 60 per cent slag content have been reproduced in the laboratory, with the procedure already described. Compressive strengths of cements have been evaluated in mortar without any additive, and by adding in mixing water a performance enhancer of the Mapei MA.P.E./S series, at a dosage of 0.2 per cent on the weight of cement. Considering that the fineness of CEM I and slag is always the same, any benefit obtained from the additive is related to the chemical effect on hydration.

The results (expressed in terms of percentage increase of strength, with reference to the mortar prepared without additive) are reported in Figure 2. As the amount of slag increases, the positive effect of additive becomes more evident and the gain in compressive strength more pronounced.

It is interesting to take into account the percentage decrease in strength as the slag content increases, in comparison to CEM I (Figure 3: one-day, Figure 4: 28-days), because this can give an idea of the possibility of clinker reduction. Looking at Figure 3, it can be seen that an increase in slag from 0 to 10 per cent and from 10 to 20 per cent leads respectively to decreases in strengths of about 12 per cent and 30 per cent. If MA.P.E./S is added, there is no loss of strengths if 10 per cent clinker is replaced by slag, and the reduction of 20 per cent clinker leads to about 15 per cent loss, rather almost 30 per cent without any additive. As a matter of fact, it is possible to produce a cement with a higher slag content, while keeping the mechanical performances closer to pure Portland cement.

Conclusion

In the European cement industry the use of blended cements is growing strongly thanks to the fact that the reduction of carbon dioxide emissions forces the reduction of clinker use.

Blast furnace slag cements are very interesting because they present several advantages, such as reduced heat of hydration and improved resistance to chemical attack. On the other hand, the lower clinker content affects compressive strengths, particularly at early ages.

The use of chemical additives usually increases the hydration degree of clinker. As a consequence, a higher amount of slag reacts with portlandite giving calcium silicate and aluminate hydrates. In slag cements, the chemical effect of MA.P.E./S becomes more evident as the slag content increases.

The use of MA.P.E./S grinding aids allows interesting clinker reduction, lowering the decrease in compressive strengths given by clinker reduction.

References

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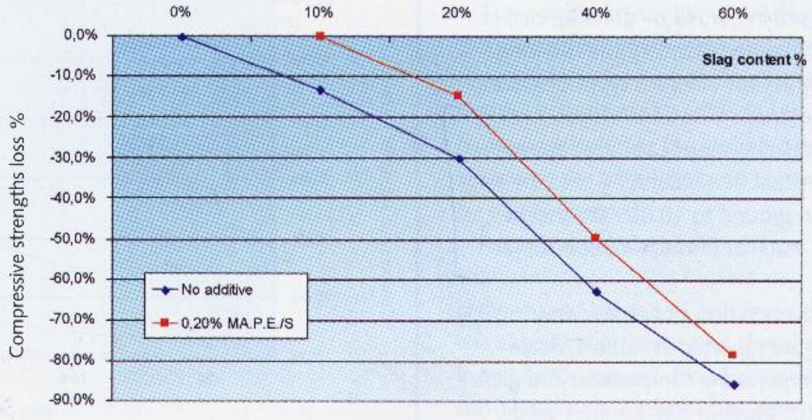

Figure 4: 28-days compressive strength decrease vs slag content with and without MA.P.E./S