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**Improved Performance of Granulated Blastfurnace Slag (GBS)
Cements with Cement Additives**
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Abstract

Despite the diffusion of slag cements on the markets, there is a lack of articles in the literature which discuss the behaviour of slag in the presence of cement additives. Mapei R&D laboratories have therefore decided to study the effects of grinding additives on slag cements in terms of the grinding aid effect and the increase of mechanical strengths.

Four GBS, representative of European slag production, have been chosen for testing purposes coming from steel plants in different countries (Italy, Poland, Slovakia and the Czech Rep.).

These GBS were characterised by means of chemical analysis. Meanwhile their grindability and hydraulic behaviour have been examined using various analytical techniques (Temperature profile of cement hydration, XRD, ESEM-FEG).

An investigation of the behaviour of these GBS within CEM III/A cements reproduced using a reference clinker (characterised by a high C_3A and C_3S content) was performed through a series of laboratory grindings of various samples, with and without grinding additives. Mechanical-physical analysis in terms of fineness and strengths and chemical analysis in terms of temperature profile, ESEM_FEG were performed on these cements.

Beyond the well known grinding aid property it clearly emerges from the data collected that the additives have a marked effect on the hydration and hence the development of the mechanical strengths. A predominant strength increase effect is observed at the early ages (1 and 2 days) which is maintained as the hydration of the slag itself gradually initiates.

INDEX

Introduction	Page	1
--------------	------	---

PART ONE

Characterisation of slag	Page	3
- Basicity Index and Glass Content		
- Selected GBS		
- Chemical Analysis		
- Glass Content		
- Elementary analysis		
- Grindability of 4 GBS		
- Morphological analysis of hydrated products		
- Temperature Curves		

Conclusion – first part	Page	10
-------------------------	------	----

PART TWO

Interaction with Cement Additives	Page	11
- Slag cement		
- Cement Additives		
- Temperature profile		
- Benefits from Cement Additives		

Conclusion – second part	Page	18
--------------------------	------	----

Bibliography	Page	19
--------------	------	----

Introduction

The utilisation of Granulated Blastfurnace Slag (GBS) in the production of cement has become well established, from the start of the previous century, due to the physical and chemical characteristics of this material (since 1909 the German standards permit the use of slag in the production of cement). It is well known that granulated blast furnace slag (GBS) is a valid constituent for durable cements: the hydraulic properties and in some cases the economical advantages, have permitted the production of cements where slag content can vary from quite low percentages up to levels where the clinker content is abundantly surpassed. The large scale availability of this material, especially in certain geographical areas, has led to the widespread diffusion of slag cements (CEM III, according to the European Standard EN 197-1). In Europe (2001) the amount of CEM III type constitutes 6,5 % of the total production and when we sum the production of CEM II/A-S and II/B-S types (Portland Slag Cements) the total amount reaches 10,7 %.

If we consider that today the majority of GBS in Europe is dedicated for use in the cement industry and ready to use mortars, it is quite common for industry to supply to the market slag with characteristics “ad hoc” for cement production: slag is no longer seen as a waste product, but as a fundamental component for the production of durable cements with a high resistance to chemical aggression. In this context cement producers can find on the market GBS characterised by different performances and characteristics, which may be matched with specific requirements (type of clinker, market etc.).

Traditional advantages of slag cements with respect to Portland cements are greater resistance to chemical aggression, the low heat of hydration and economics savings. Also as a result of the necessity to limit the emissions of CO₂ (and hence to reduce the expenditure for the related taxes) in Europe, the production of cements with a reduced content of clinker is generating an ever growing interest.

The disadvantages are the difficulty in grinding (slag is hard and often abrasive) and the poor early strengths. This final problem has become more important in recent years given that the construction industry has become more orientated towards the use of cements having high strengths at 1 and 2 days.

In this context cement additives may find the grinding of slag cements a fertile field for their application, given that they are able to eliminate the typical disadvantages of GBS cements (helping to grind and increase early strengths) while maintaining the benefits.

Part one**CHARACTERISATION OF SLAG****Basicity Index and Glass Content**

Slag used in the production of cement is the “final product” from the steel making process which is rapidly cooled, so that it may assume a glass like (vitreous) form and a granular appearance. The evaluation of the hydraulic activity of the slag is a problem which the cement producer must consider and which is necessary in order to forecast the mechanical performances of the cement produced with slag.

Guidelines are provided in the national standards. For example the European Standards define the characteristics of a slag which is suitable for use in cement plants as follows:

-An index of basicity. The most common modulus is expressed as $(\text{CaO}+\text{MgO})/\text{SiO}_2$, and must be greater than 1. The most active GBS normally have values greater than 1,2.

-The sum of the three principal constituents $(\text{CaO}+\text{MgO}+\text{SiO}_2)$, must be greater than 2/3 of the mass in weight. In our case, the four selected GBS have the parameters in Tab. 1.

Tab.1 – Basicity Index

GBS Identification Number	$(\text{CaO}+\text{MgO})/\text{SiO}_2$	$\text{SiO}_2 + \text{CaO} + \text{MgO}$
P 467	1,31	87,07
C 543	1,25	89,25
S 603	1,28	88,08
I 598	1,34	82,50

Another aspect to consider is the glass phase content. In order to ensure the development of the hydraulic properties it is fundamental that the slag is cooled rapidly (tempered). In this way the structure of the material will be glass like (vitreous) with a high energy potential and not crystalline and more stable with a low energy potential.

Tab. 2 – Glass content

	P 467	C 543	S 603	I 598
Glass content %	97,9	84,1	92,3	100
Crystalline content %	2,1***	15,9**	7,7*	-

Note:

* Type of mineral: merwinite

** Type of mineral: melilite + merwinite

*** Type of mineral: merwinite + C_3S

Method: XRD + Rietveld

The parameters previously described, while useful for the characterisation and correct identification of different GBS, they do however require the use of appropriate analytical techniques and as a consequence time and dedicated resources. Even if they are not exhaustive (they do not take into account all the constituents which sometimes are minor but important), they can indicate if a slag is hydraulically active and are an index of the effective contribution of a slag to the development of the strengths of a cement.

In practice in order to evaluate a slag for use in cement plants, it is still quite common to test mechanical strengths in mortars, where a certain percentage of clinker is substituted with the equivalent percentage of slag. The advantage of this procedure is that it is rapid and the interactions between clinker and the slag are taken into account.

Selected GBS

We have selected four European GBS which are currently used in cement plants, three of which come from Central Europe where slag cements are very common and one Italian slag. The identification numbers are: P467 from Poland, C 345 from Czech Rep., I 598 from Italy, S 603 from Slovakia.

All four GBS had a granular appearance, with slight differences in colour and particle size. These are characterised by a compact structure and not “porous”, with a low tendency to retain humidity. Notwithstanding the limitations expressed above, we will try to characterise, from a chemical and physical point of view, these 4 GBS before moving forward to analyse their behaviour with clinker and in the presence of cement additives.

In order to reproduce a cement in the laboratory mill we chose a clinker characterised by having high C_3A and C_3S contents which, because of its intrinsic characteristics (high early strengths and high calcium hydroxide liberated into solution), matched well with a “slow” material such as slag.

Chemical Analysis

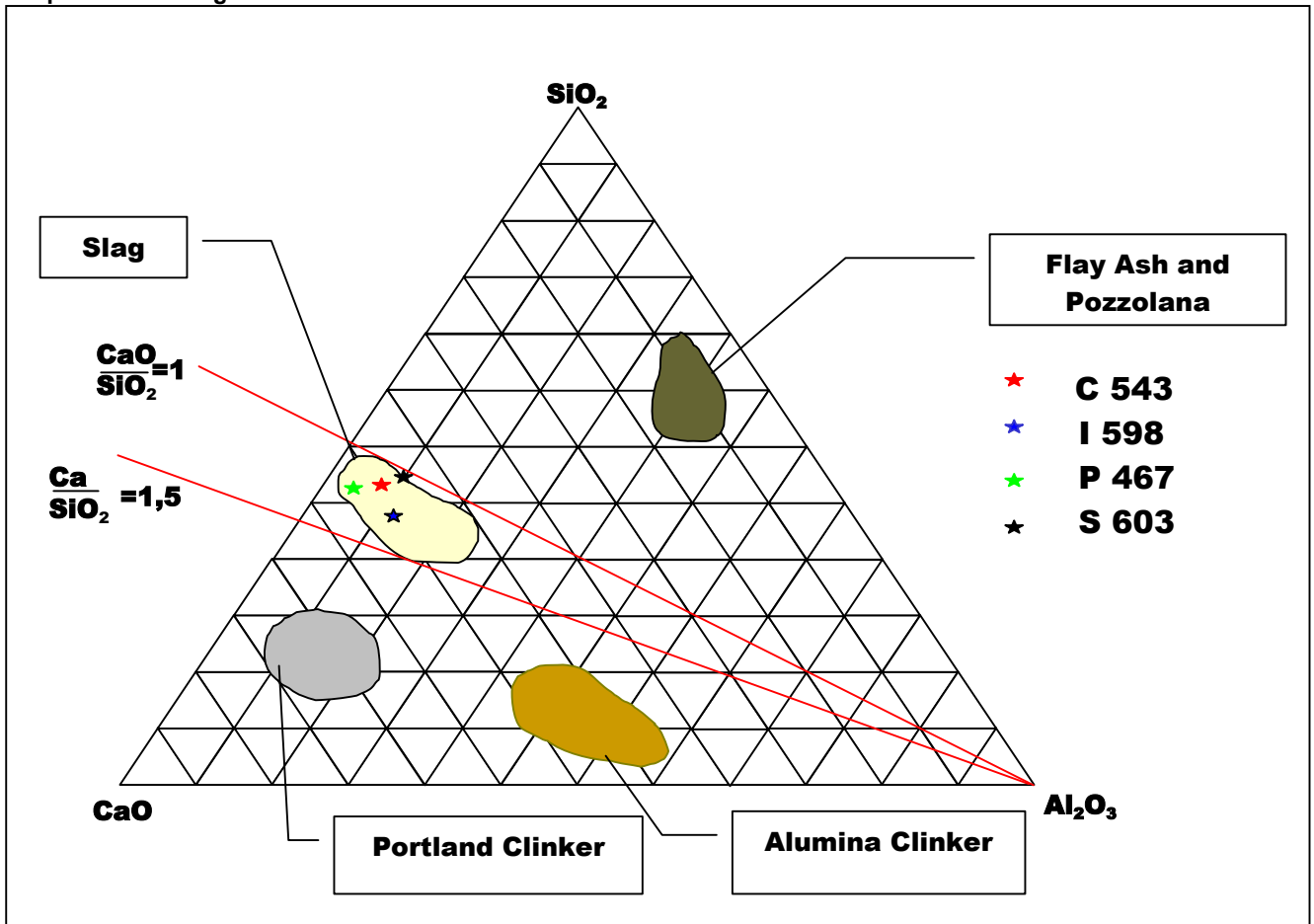
Before considering the elementary constituents of the four selected GBS, we have inserted them in a ternary diagram $\text{CaO} - \text{SiO}_2 - \text{Al}_2\text{O}_3$ (like that proposed by Keil) in order to determine their position in relation to the other hydraulically active materials currently utilised in cement plants. In this type of diagram we make the hypothesis that the materials are composed 100% by CaO , SiO_2 , Al_2O_3 .

The selected GBS are positioned very close to one another. Only number I 598 differs slightly from the other characterised by a superior content of Al_2O_3 with respect to the other oxides. It must be noted however that in a diagram of this type the content of MgO is not taken into account, but is quite important in the case of slag.

However it is interesting to note the position of the GBS with respect to the Portland clinker (characterised by a higher CaO/SiO_2 ratio) and to the pozzolana/fly ash and alumina cements, which in general contain more Al_2O_3 and have different CaO/SiO_2 ratios.

We also have indicated the “simple” basicity of the chosen GBS, considered as $(\text{CaO}/\text{SiO}_2)$ which, except in one case (slag C 543), are greater than 1.

Graph. 1 – Keil diagram



Glass Content

An important parameter to be considered is the glass content of a GBS; X-ray diffraction is an analytical technique which permits a correct interpretation of this parameter and which also allows any further crystalline phases present to be identified.

The 4 GBS shown here have the following glass contents:

P 467: 97,9%
C 543: 84,1%
S 603: 92,3%
I 598: 100%

In this case, where different GBS are confronted, the slag I 598 is the only one with a 100% glass content and will reveal itself to be the most hydraulically active (it is also that which has the highest basicity index). The C 543 slag is that which was cooled in the least efficient manner and therefore can not fully express it's hydraulic properties.

Elementary analysis

The table n°3 shows the elementary analysis of the four GBS.

Tab. 3 – Elementary analysis

			Cement Additives Division			MAPEI GRINDABILITY TEST			088/2004	
Sample identification			Chemical analysys							
ID number	Plant	s.g.(g/cm3)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Mn ₂ O ₄	(CaO+MgO)/ SiO2	SiO ₂ +CaO+MgO
P 467	P	2,817	37,67	5,89	1,61	43,79	5,61	1,12	1,31	87,1
C 543	C	2,878	39,75	9,95	2,56	39,07	10,43	0,40	1,25	89,3
S 603	S	2,879	38,68	7,35	0,79	41,27	8,13	0,98	1,28	88,1
I 598	I	2,837	35,28	10,63	0,92	40,73	6,49	1,10	1,34	82,5

The chemical analysis of the GBS show that the compositions are similar, in particular regarding the CaO content. Meanwhile more significant differences may be seen in the SiO₂ content. In one case the CaO content is slightly lower than that of the SiO₂; this however is compensated by a high MgO content. In one single case the Al₂O₃ content exceeds 10%.

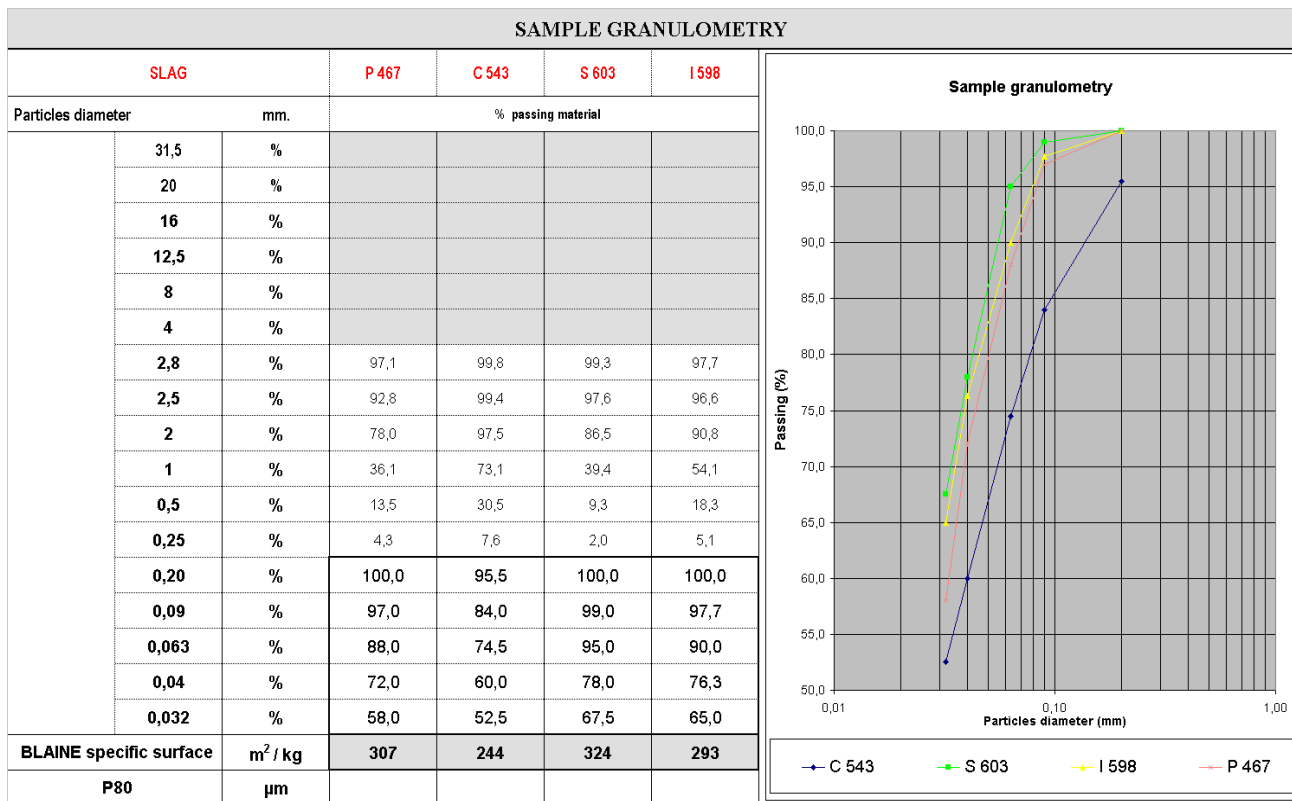
On the right-hand side the Basicity modulus are reported. The GBS are divided into two groups: Numbers I 598 and P 467 have a modulus greater than 1,3 while the other two are around 1,2.

The sum of the $\text{CaO} + \text{SiO}_2 + \text{MgO}$ in three cases is greater than 87% while the slag numbered I 598 is around 82%.

Grindability of 4 GBS

The grindability of the four 4 GBS was also evaluated. This is another important parameter for cement plants: the specific energy consumption in relation to the fineness of the cement is dependant on this parameter.

Tab. 4 – Grindability of 4 GBS

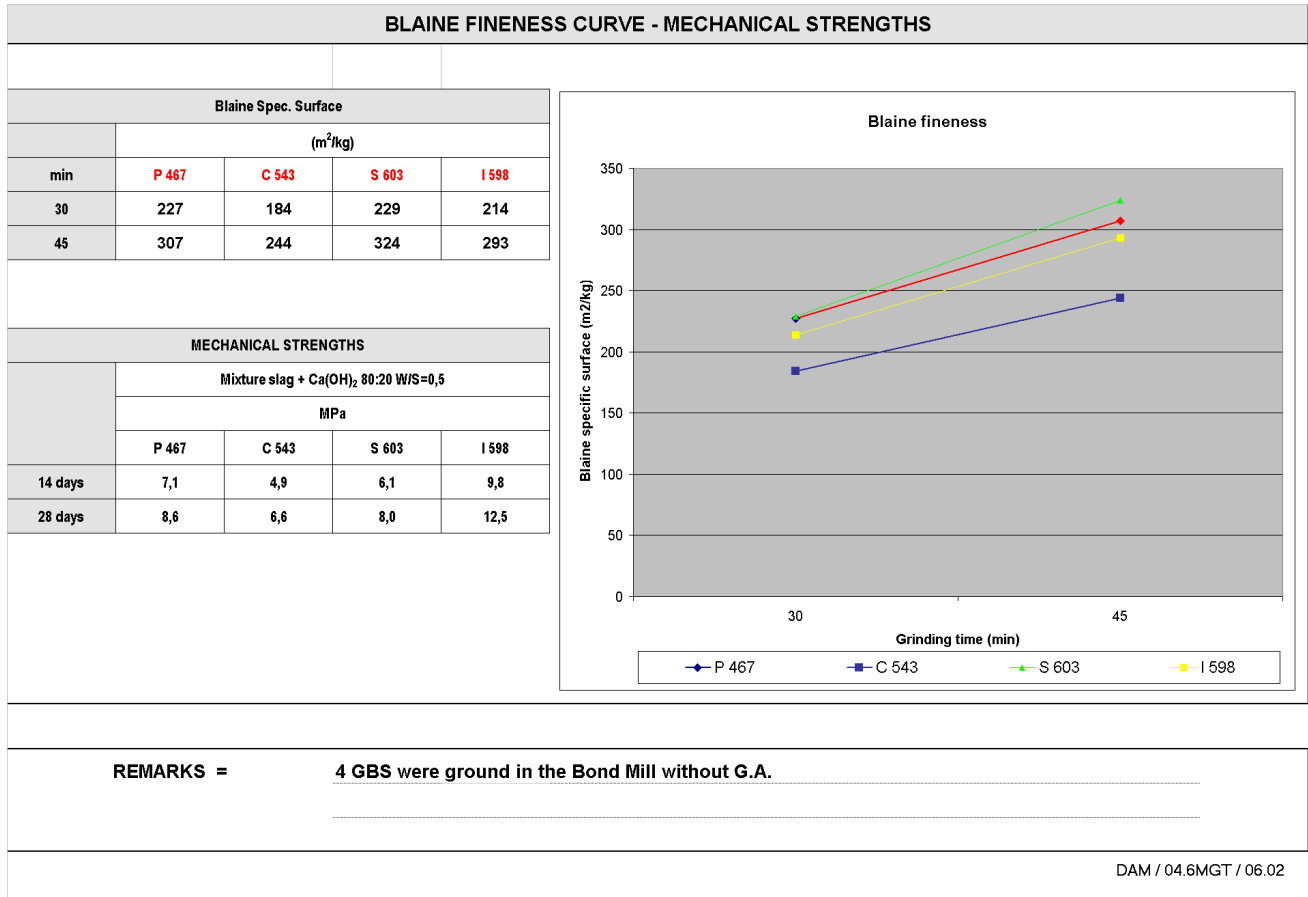


The GBS were dried at 80°C for 24 hours and then ground in a Bond type laboratory mill to a fixed time (45 min). The tests were repeated to obtain reliable average data.

The grindability of the four GBS is different, as may clearly be seen from the Alpine residuals. In particular the slag C 543 is the hardest, while the slag S 603 is the softest. The laser curves confirm the Alpine data, while the Blaine values show two GBS (P 467 and I 598) inverting their respective positions, signalling that the coating tendency of these materials is different.

The Tab. 5 illustrates the increase in Blaine as the grinding time is increased from 30' to 45'. In one case (S 603) the angle of the curve is different from the others, signifying a different rheological behaviour of this material.

Tab. 5 – Blaine development and Strengths



On the left side we have the mechanical strengths of the four GBS.

Each slag was hydrated (without clinker) with calcium hydroxide as an activator, in order to verify it's reactivity. The strengths obtained show that we can divide our GBS into two groups, independent of fineness: I 598 and P 467 with higher strengths and S 603 and C543 with lower strengths. This behaviour will repeat itself even when we'll reconstruct cement (slag + clinker). It should be emphasised that the 2 GBS with higher strengths are characterised by higher Basicity index and higher glass content.

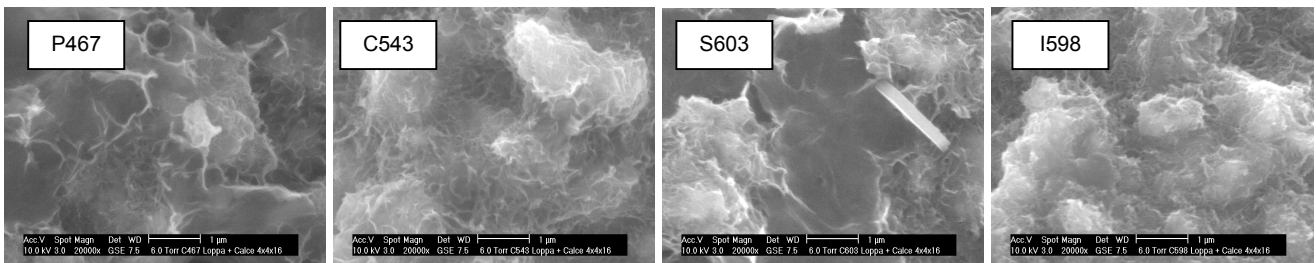
Morphological analysis of hydrated products

Each mortar was analysed at 28 days with a ESEM-FEG electron microscope, in order to identify the structure and the hydrated products.

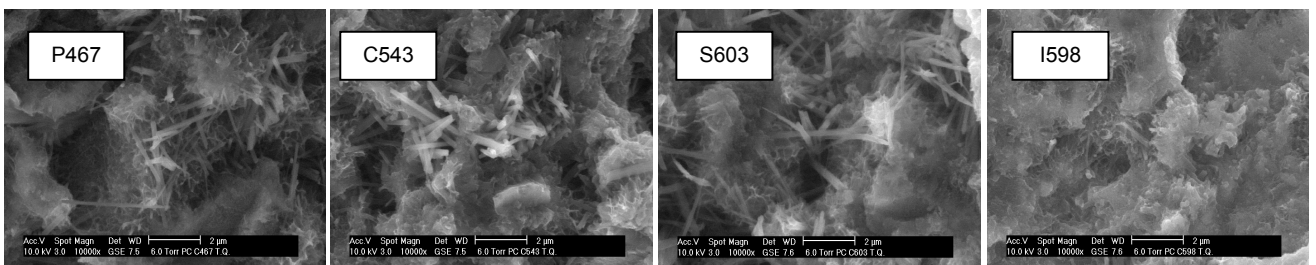
The following photos show the hydration of the GBS (slag and calcium hydroxide $\text{Ca}(\text{OH})_2$ as an activator).

In the first series of pictures one does not see, with the exception of slag n° S 603 and only in a minimal way, the presence of ettringite, as expected given the absence of sulphates. With the addition of clinker and gypsum (second series of pictures) we can see that things change completely.

Pict. 1 – 28 days hydration GBS + calcium hydroxyde



Pict. 2 – 28 days hydration CEM III/A 32,5 R with the 4 GBS

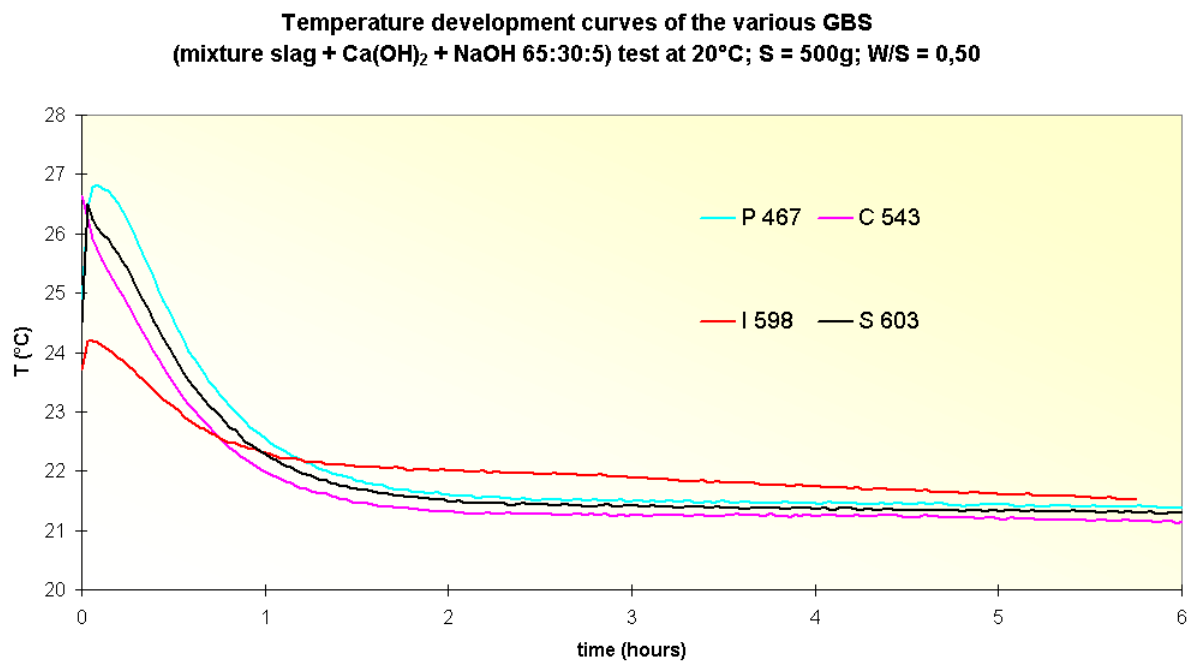


Temperature Curves

The heat developed during hydration is an indication of the hydraulic activity of the slag. These curves in which we may see the first hours show an initial peak similar for three of the GBS, meanwhile the I 598 develops lower heat during the first hours of hydration. This tendency is however inverted afterwards.

In any case the total heat developed by the two GBS, I 598 e P 467 in the arc of 48 hours (end of our test) is superior to that developed by the other two GBS characterised by inferior mechanical strengths.

Graph. 2 – Temperature development curves



Conclusions – first part

We may summarise the data collected during the characterisation of the GBS in the following manner:

- 1) The **mechanical strengths** of the GBS may be divided into two groups: I 598 and P 467 with high mechanical strengths, S 603 and C 543 with low mechanical strengths. The two GBS with the higher strengths also have a higher Basicity index: 1,3 versus 1,2 and in the first 48 hours develop a greater quantity of heat. They also have a higher glass content.
- 2) As regards the **grindability** one can clearly identify a slag which is harder than the others (C 543) and one which is more easily ground (S 603), even though close to the other two intermediate GBS. There is not a direct correlation between the grindability of the GBS examined and the mechanical strengths that they develop: we may affirm with regards to the strengths that it is the “chemical “ aspects which prevail.

Part two**INTERACTION WITH CEMENT ADDITIVES****Introduction**

The grinding of slag cements often presents some problems related to the slag itself, which in general is difficult to grind and abrasive. There are three categories of grinding additives which may be employed on slag cements:

- 1) Pure grinding additives: **G.A.** (e.g. MA.G.A./C 098)
- 2) Grinding additives with a chemical effect on strengths: **G.A. +** (e.g. MA.G.A./C 150)
- 3) Performance Enhancers, specifically formulated to reduce the clinker content: **P.E.** (e.g. MA.P.E./S 500)

As the summary Tab. 6 shows, all three additive categories are characterised by having an excellent grinding effect (production increase). While this is the principle function for the **G.A.**, for the **G.A. +** the increase in the mechanical strengths is equally important, with a possible reduction of clinker content. However when the clinker reduction is the principle objective, the most suitable additives are those of the **P.E.** category which give the best results.

Tab. 6 – Grinding effect and Strengths

	G.A.	G.A. +	P.E.
Production Increase	+++	+++	+++
Strengths Increase	+	++	+++

Slag cements

For each slag, we have reproduced in a laboratory mill a cement, type CEM III/A 32,5 R (50% slag, 45% clinker, 5% gypsum), introducing into the system the same energy (same grinding time) with and without cement additives. The mineralogical composition of the clinker is given in the tab. 7.

Tab. 7 – Mineralogical clinker composition %

C₃A	C₃S	C₂S	C₄AF
11,90	67,12	8,14	8,00

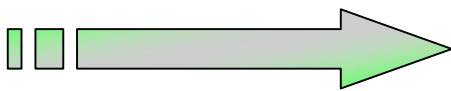
After 45 minutes of lab grinding, it is interesting to notice that the results in terms of fineness and strengths are very different.

This shows that, translating this experiment into an industrial case, we should vary the fineness (and the mill output) in order to produce a cement with determined strengths. Consequently using the 4 considered GBS, we will have different cement production costs. In practice cement factories are often obliged to use a specific GBS (due to availability, price etc.); in these cases Cement Additives come into play, contributing in a decisive manner to obtain the desired results with the lowest production costs.

Graph. 3 – Lab slag cement reproduction

Input:

- same raw materials
- same energy (same grinding time)
- cement additives (with and without)



Output:

- cement (same composition)
- **different fineness**
- **different strengths**

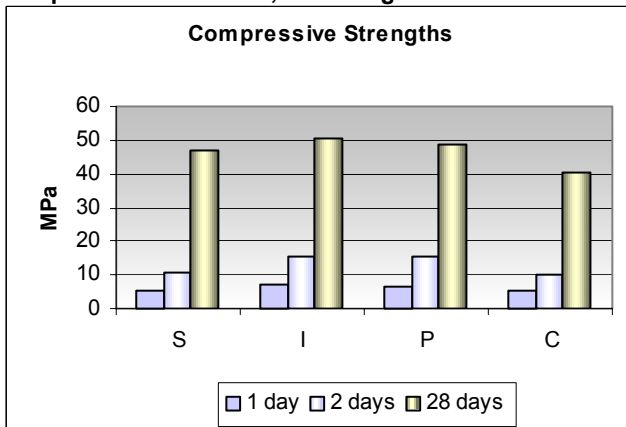


The following table and graphs show the strengths and the fineness obtained with each slag, **without additives**, using the same reference clinker. As in the case without clinker, one may see from the strengths (e.g. at 2 days) that the materials under examination divide themselves into two groups: those with mechanical strengths around 10 MPa (C 543 and S 603) and those which reach 15 MPa (I 598 and P 467).

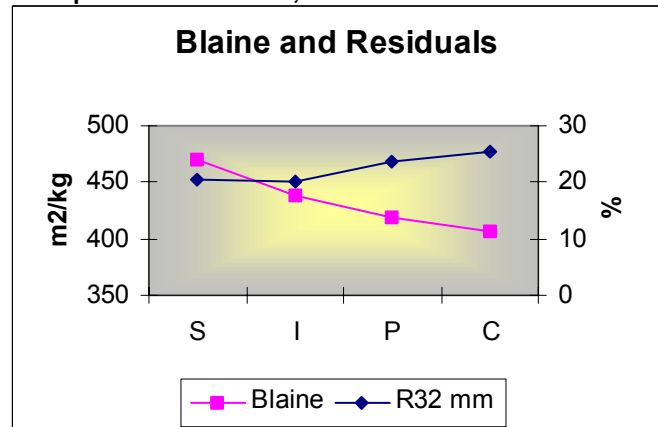
Tab. 8 – CEM III/A 32,5 R average strengths

	S 603	I 598	P 467	C 543	Average
1 day	5,2	7,5	6,5	5,5	6,2
2 days	10,4	15,7	15,3	10,2	12,9
28 days	46,7	50,4	48,8	40,4	46,6

Graph. 4 – CEM III/A 32,5 R strengths



Graph. 5 – CEM III/A 32,5 R fineness

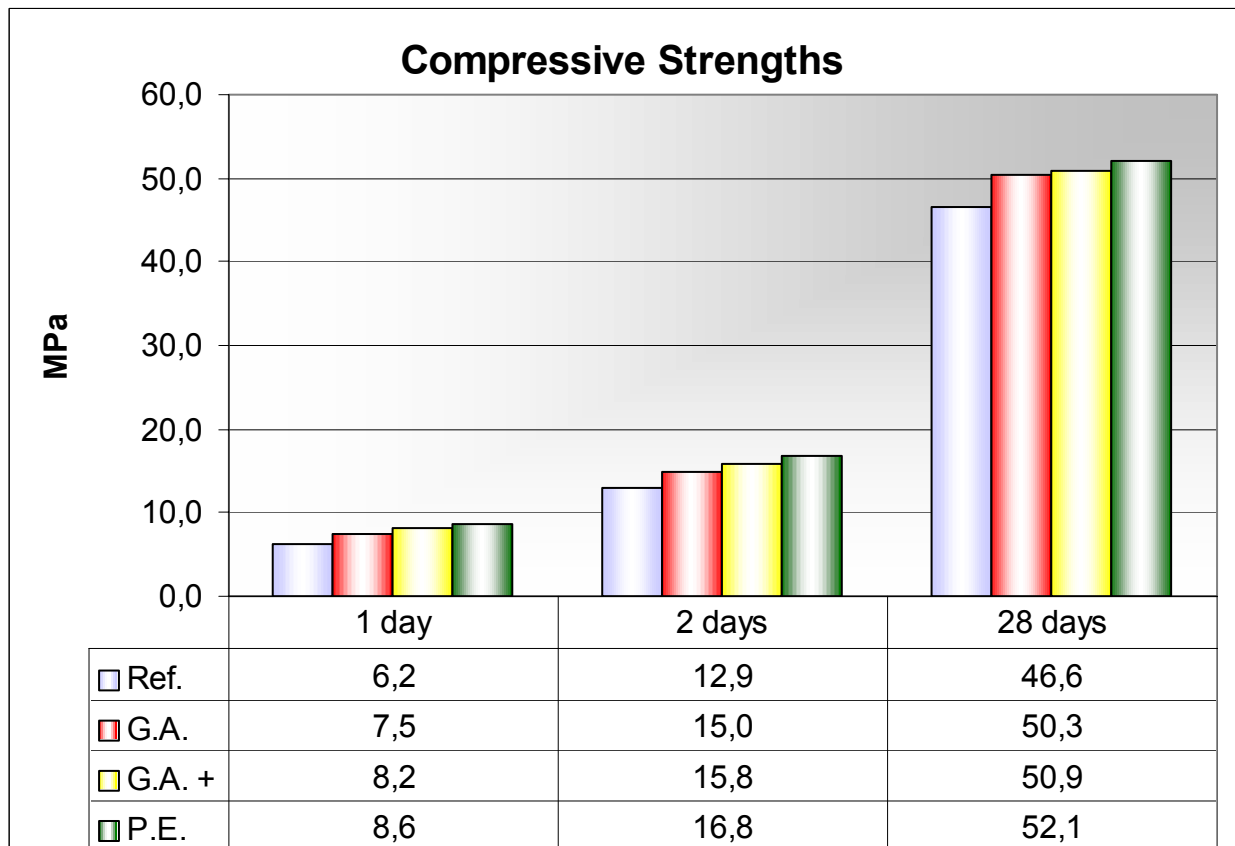


In the presence of clinker the same ranking is once again obtained: with the better performing GBS, the best cements are produced. The levels of fineness, once more characterised by the hardness of the GBS, are indicated in the Graph. 5 (residues at 32 μm and Blaine).

The Graph. 6 shows the average results obtained grinding the cement produced with the 4 GBS, with and without *Cement Additives*. These values may be commented as follows:

- with the **P.E.** the increase in strengths with respect to the additive free situation (ref.) is 39% at 1 day, 30% at 2 days and 11% at 28 days.
- with the **G.A. +** the increase in strengths with respect to the additive free situation (ref.) is 32% at 1 day, 22% at 2 days and 9% at 28 days
- with the **G.A.** the increase in strengths with respect to the additive free situation (ref.) is 20% at 1 day, 16% at 2 days and 7% at 28 days

Graph. 6 – CEM III/A 32,5 R strengths



Detailed results, expressed in MPa, are shown in the Tab. 9:

Tab. 9 – CEM III/A 32,5 R mechanical strengths with 4 GBS and Cement Additives

Reference					G.A.				
	S 603	I 598	P 467	C 543		S 603	I 598	P 467	C 543
1 day	5,2	7,5	6,5	5,5	1 day	6,8	9,1	7,3	6,6
2 days	10,4	15,7	15,3	10,2	2 days	14,1	17,1	16,2	12,5
28 days	46,7	50,4	48,8	40,4	28 days	52,5	51,8	52,2	44,7

G.A. +					P.E.				
	S 603	I 598	P 467	C 543		S 603	I 598	P 467	C 543
1 day	7,6	10,0	8,1	7,2	1 day	9,0	10,2	7,6	7,7
2 days	14,8	17,6	16,4	14,2	2 days	16,9	17,8	16,6	15,7
28 days	52,0	54,2	53,3	44,0	28 days	54,0	54,2	52,9	47,1

These very interesting results illustrate how the use of cement additives (and in particular the P.E.) in slag cement may be transformed into a competitive advantage of primary importance.

When we look at the results obtained with each single GBS one may principally observe:

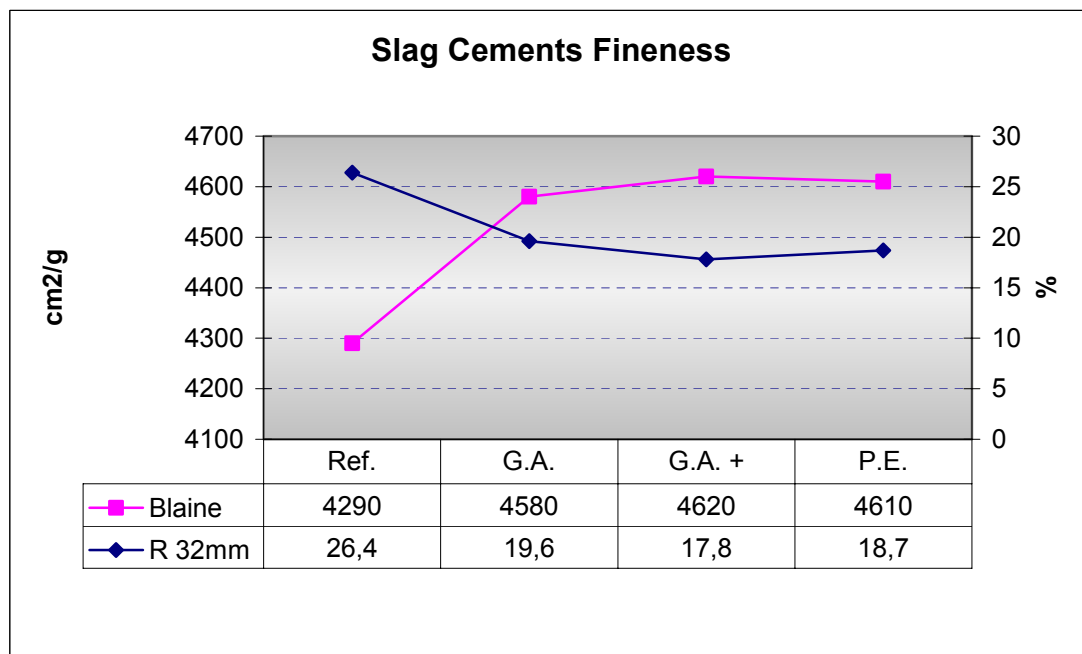
- 1) The highest percentage increases of the strengths are in general obtained by using the cement additives with the GBS C543 and S 603, characterised by having lower strengths.
- 2) The cements produced with GBS characterised by having higher strengths (I 598 and P 467), also have higher strengths with and without cement additives. In particular the cement with slag I 598 has the highest strengths in all cases.
- 3) With the use of cement additives we can bridge the gap between the low and high performance GBS.

Cement Additives

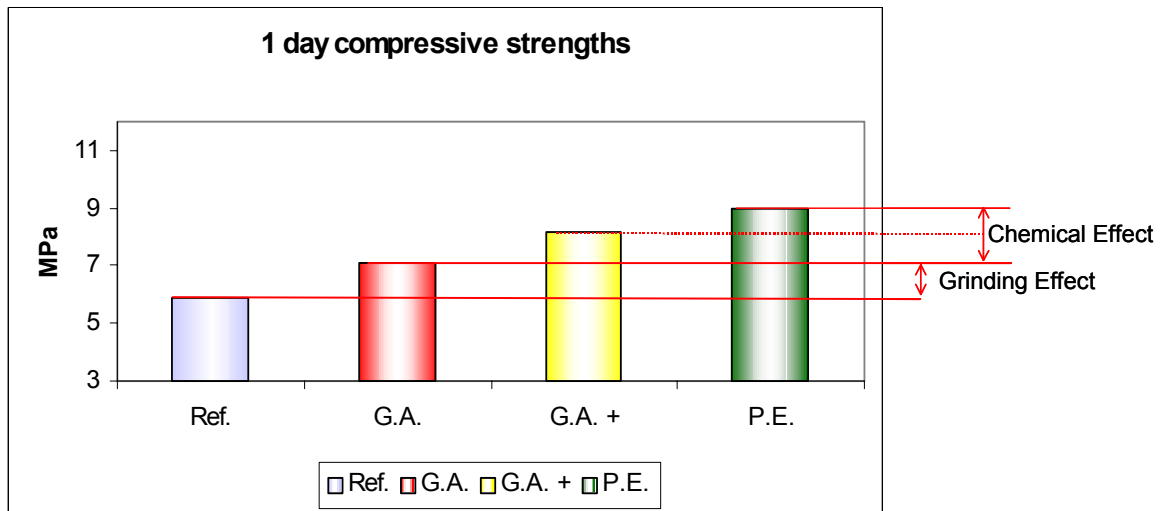
If one considers the average strength increases obtained with the three grinding additives with respect to the reference (additive free), we may distinguish the increase obtained thanks to the higher level of fineness (and the different particle distribution) from that obtained thanks to the chemical effect of the additives.

In particular one can see that the increase in fineness obtained with the three types of additives is very similar (as said before they are characterised by having the same level of grinding aid effect), both in terms of Blaine (approximately + 300 cm²/g with respect to the reference) and residues (-26% at 32 µm with respect to the reference). The Graph. 7 shows the average results obtained with the 4 GBS for each category of cement additives.

Graph. 7 – CEM III/A 32,5 R average fineness

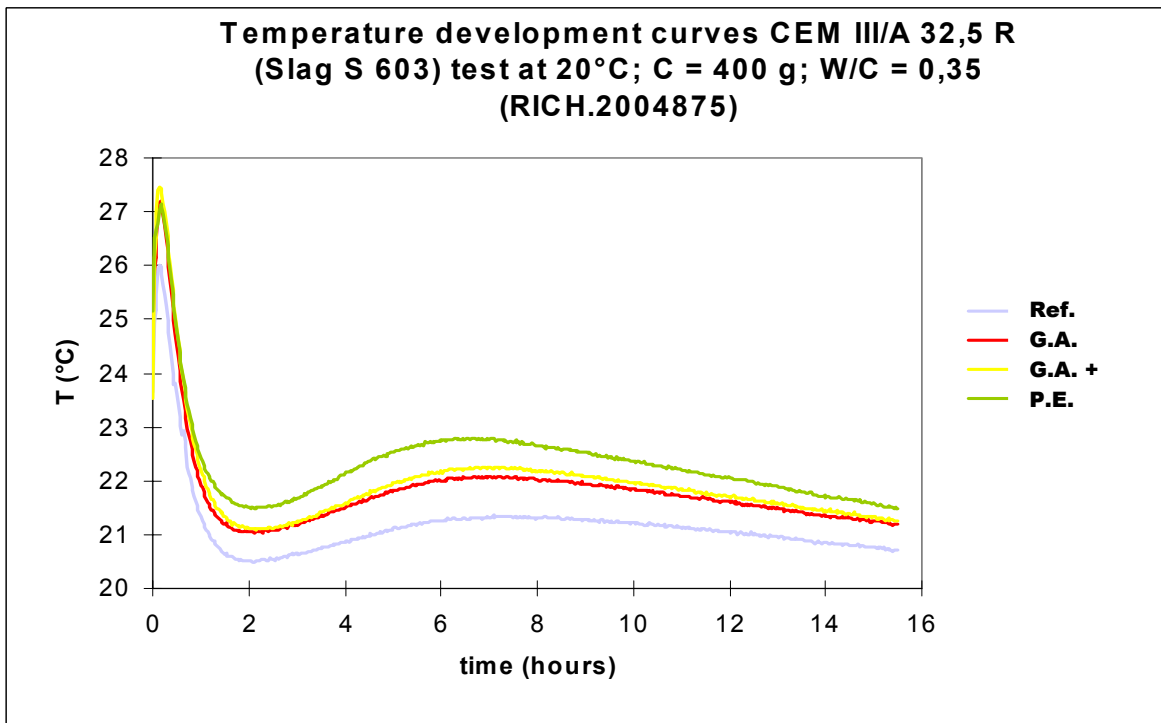


Given that the three additives have approximately the same grinding effect, the strength increase related specifically to the chemical effect (for P.E. and G.A. +) is given by the difference between the total strength increase and the “grinding effect”. Normally the “grinding effect” is used to increase the hourly production (t/h) of the mill, while the “chemical effect” is used to increase the strengths or the percentage of slag in the cement at equivalent strengths.

Graph. 8 – Strengths: “grinding effect” and “chemical effect”

Temperature profile

Here we now show, for example purposes, the temperature development curves for the cement produced with one of the four GBS (S 603), where one may clearly see that the development of heat associated with the use of Cement Additives is definitely higher with respect to the reference (in particular where the P.E. type additives were used).

Graph. 9 – CEM III/A 32,5 R temperature development curves with Cement Additives

This result, as logic would expect, is exactly in line with the development of the mechanical strengths.

Benefits from Cement Additives

Usually with slag cements the increases in production obtained may vary from 5% to 20%, in function of:

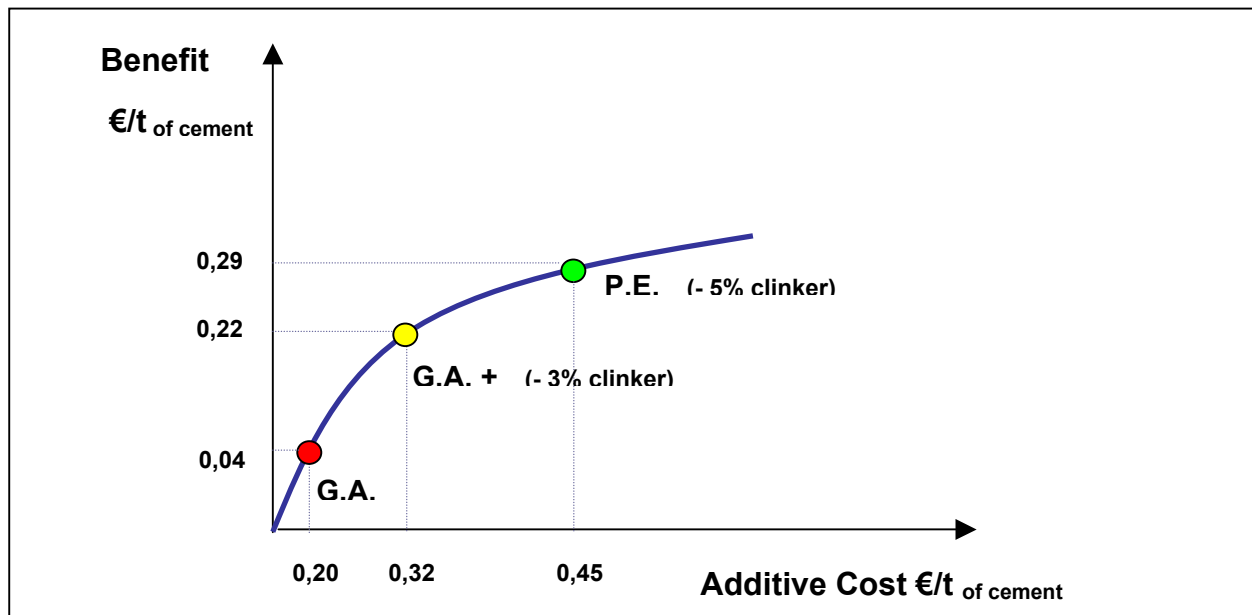
- the level of fineness of grinding
- the type of mill-separator circuit
- the nature of the materials to be ground.

Let us now consider an industrial mill producing slag cement where the percentage increase in production with cement additives is around 10% at fixed fineness and quality.

From different types of cement additives we can get the following benefits:

- **G.A.**
 - +10% increase in production
 - total savings: 0,04 €/t_{of cement}
- **G.A. +**
 - +10% increase in production
 - – 3% clinker content
 - total savings: 0,22 €/t_{of cement}
- **P.E.**
 - +10% increase in production
 - – 5% clinker content
 - total savings: 0,29 €/t_{of cement}

Graph. 10 – Benefits from Cement Additives



Notes:

- a) Additive cost/t of cement: 0,20 €/t, 0,32 €/t, 0,45 €/t
- b) Additive dosage: 0,03%, 0,04%, 0,20%
- c) Energy cost 0,06 €/kWh, specific power consumption 40 kWh/t
- d) Energy saving: 0,24 €/t
- e) Difference between clinker and slag cost: 10€/t

Conclusions – second part

- 1) - Cement Additives are ideal for the production of slag cements, as they permit improved grinding as well as strength increases at all ages and in particular at early ages, thus eliminating the typical problems related to these cements.
- 2) - The GBS available on the markets are different from one another in terms of their performances. Practical tests still remain useful for an evaluation of a slag. Even though the chemical and physical characterisations require sophisticated analytical techniques they do however provide valuable information regarding the hydraulic activity of slag.
- 3) - Cement Additives suitable for use on slag cements belong to three categories:
 - G.A. to be used when the principal objective is to increase the mill production
 - G.A.+ to be used when the principal objective is to improve the quality of the cement
 - P.E. to be used when the principal objective is to reduce the clinker content



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