Fly ash cements: correlating cement additives performance with chemical composition of fly ashes

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Abstract

Supplementary cementitious materials keep increasing their importance worldwide. Fly ash, blastfurnace slag, limestone, natural pozzolanas can substitute clinker in cement composition, improving sustainability and economics of cement manufacturing. However, their use can lead to a loss of performances (namely strengths) that limits the maximum amount of clinker substitution.
The present study would like to be the start of a thorough practical understanding of the effect of high substitution by fly ash. Effects on strength have been studied for several fly ash and clinker combinations, correlating performance to chemical composition.
In addition, treatment of fly ash cements with chemical additives (grinding aids/quality improvers to be added during cement manufacturing) has been studied. This allows the recovery of the decreased performances, opening the door for higher substitutions of clinker without losing strength.
In conclusion, the results can provide insight on specific fly ash selection by a cement manufacturer, in combination with chemical enhancers of the hydration.

Originality

To the authors' knowledge, no previous studies of this type exist of the correlation between chemical and mineralogical composition of fly ashes, in combination with chemical additives, and the properties of finished blended cement.

***Keywords**:*
Cement; fly ash; clinker; SCM; chemical additives

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1. Introduction

As it is well known and reported in many occasions, one of the most effective ways to lower the manufacturing cost of cement is by lowering the clinker factor. Clinker is the single most expensive component of cement, due to the high-energy process required to obtain it in the kiln. Many standards all over the world allow for the manufacturing of blended cements, where part of the clinker is substituted by supplementary materials as limestone, fly ash, or blastfurnace slag. These secondary materials are directly ground together with clinker and gypsum, or milled in a separate stage, followed by blending with ordinary Portland cement. Each of them provides advantages and disadvantages (related to cost, grindability, chemical reactivity, availability) that can drive their specific application.

Fly ash is one of the most widely available supplementary cementitious materials, being the byproduct of coal burning in power plants. During the burning, fused fine particles are carried away by the flue gas and solidify by cooling to glassy amorphous ash particles with a glass content of approximately 60-85% in weight (Lutze and vom Berg, 2004). Composition in terms of crystalline phases and chemical elements has been investigated by many authors (e.g. in Prause, 1991, Richartz, 1984 and Kautz and Prause, 1986). Hydration reaction in alkaline conditions is the phenomenon that allows their extensive use as a clinker replacement: overly simplifying, this consists in the reaction of amorphous silica contained in the ashes with the calcium hydroxide produced by the hydration of cement clinker. This means that the effectiveness of the ashes in providing strength through the formation of C-S-H gel is mainly focused at later ages, since some time is needed to thoroughly spread the presence of $Ca(OH)_2$ in the matrix of cement to get it reacting with the fly ash particles. Hence, blended cements based on the substitution of clinker with fly ashes usually suffer from lower early strengths (Fraay, 1990, Huettl, 2000, Lee C. Y. *et al.*, 2003, Mueller *et al.*). Several studies have been published regarding the activation of fly ash through chemical compounds, both inorganic (e.g. alkali sulphates) and organic (e.g. alkanolamines) (Gartner and Myers, 1993, Sandberg, 2008, Scholze, 1977). In particular, triethanolamine (TEA) has been the subject of several investigations regarding the activation of blended cements containing fly ashes or other secondary components (e.g. in Lee C. Y. *et al.*, 2003). Additional work has been done to try and correlate the chemical composition of fly ashes with their reactivity (Schulze and Rickert, 2011). This study was carried out by preparing artificial cement pore solutions and varying different parameters.

1.1 Purpose of the work

In the present work, we try to take a move towards the field application, by trying to investigate the possible correlations between the fly ash composition and its reactivity in blended cements, with and without the presence of chemical activators normally used in the cement industry. The chosen approach is on purpose very practical: two industrial clinkers were selected, together with four different fly ashes, analysed for their composition, ground and mixed to yield blended cements with 20% fly ash content. These cements were used to prepare EN-196/1 mortars and determine compressive strengths. Strengths were measured on blank cements and by adding chemicals in the mixing water. The strengths results were then analysed to assess any correlation.

Data obtained through this work are not conclusive: additional investigation should and will be carried out to confirm the findings and better understand the mechanism of hydration of fly ashes in their practical application as a clinker substitute.

2.Experimental

2.1 Cements and fly ashes

The following materials were selected for the investigation:

- two Portland cement clinkers (coded C4564 and C4705)
- one natural gypsum (dihydrate)
- four fly ashes (coded C4672, C4736, C4737 and C4738).

Criteria followed in choosing were to avoid very particular material, trying to focus on “typical” characteristics that could have the widest interest. The two clinkers come from different geographical areas, the fly ashes were the byproduct of different coals burned in different power plants.

Each clinker and gypsum were ground together in a laboratory mill for a standard time, in the ratio 95:5. Enough of these Ordinary Portland Cements (OPCs) was ground for all the tests, and thoroughly mixed and homogeneized to avoid any effect of fineness variation between grinding batches.

Fly ashes were used as they were received: all of them were provided “ready to use”, i.e. dry and already at a fineness compatible with direct use in cement.

Blended fly ash cements were prepared by dry blending the OPCs with each of the ashes in the ratio of 80:20, yielding 8 different cements (4 for each clinker).

For each of these 8 cements, compressive strengths were measured according to EN-196/1, so with standard water/cement ratio of 0.5 and standard sand/cement ratio of 3:1.

For the determination of strengths in the presence of chemicals, the latter were added directly in the mixing water by weighing the appropriate amount of each.

For the assessment of chemical and mineralogical composition of OPCs and fly ashes, X-Ray fluorescence (Bruker AXS S8 Tiger), thermogravimetric analysis (TGA Netzsch TG209F1 Iris) and quantitative X-Ray diffraction with Rietveld method were used. Powder diffraction data were collected with a PANalytical X’pertPro MPD diffractometer with theta–theta geometry, equipped with an X’Celerator detector working with the CuKα radiation (1.54184 Å) in the 2theta range 5–80, a step size of 0.017° 2 theta and a scan step time (s) of 102,1. All data collections were performed at room temperature with back-loading sample holders to avoid preferred orientation of crystallites. Data were analysed by the Rietveld method (Rietveld, 1969) using the Bruker AXS software package TOPAS 4.2 operated in the fundamental parameters mode (Cheary et al, 1992, Coelho, 2000, BRUKER AXS, 2003).

2.2 Chemical additions

As for chemical additions, on each cement and fly ash combinations the following were added (dosages refer to total cementitious):

- triethanolamine (TEA) at a dosage of 250 ppm
- triethanolamine (TEA) at a dosage of 250 ppm and sodium chloride at a dosage of 500 ppm
- triethanolamine (TEA) at a dosage of 250 ppm and sodium thiocyanate at a dosage of 1000 ppm

Choice of dosages was dictated by actual use of these chemicals in practical use.

These chemicals are well known in the practice of chemical strength activators for cement, and several studies are available on their effects (for example in Dodson, 1990 and references therein). However, no agreement exists on the actual mechanism of action, apart from the common acceptance that it is a catalytic type of mechanism, due to the very low amounts of chemicals required and their absent/minimal consumption. At this stage, it is not the purpose of this study to inquire further about these mechanisms.

3.Results

Results of clinker XRD-Rietveld and calculated OPC composition are reported in table 1. All values are expressed in %.

Composition of fly ashes (XRF data) are reported in table 2. All values are expressed in %.

Table 3a and 3b report all the strengths data at 1, 2 and 28 days. In addition to the absolute values in MPa, % increases over the blank are reported.

Table 1 - Composition of OPCs (XRD, TGA), %

Sample	OPC C4564	OPC C4705
C_3S M3	30.5	34.6
C_3S M1	29.0	28.2
C_2S	20.2	17.2
C_3A, cubic	4.4	4.3
C_3A, orthorombic	1.5	-
C_4AF	6.4	6.9
CaO	0.5	1.0
MgO	2.1	1.1
Gypsum (dihydrate)	2.2	2.3
Bassanite	-	0.5
Anhydrite	0.2	-
Calcite	-	0.9
Portlandite	1.0	1.2
Arcanite	1.1	0.8
Ca-Langbeinite	-	0.9
Aphtitalite	0.6	-

Table 2 – Composition of fly ashes (XRF), %

Sample	Fly ash C4672	Fly ash C4736	Fly ash C4737	Fly ash C4738
MgO	1.06	1.54	1.18	1.61
K_2O	0.62	1.76	1.74	1.45
Al_2O_3	29.61	24.29	19.32	27.72
SiO_2	51.43	57.51	60.60	50.74
CaO	5.49	3.36	1.73	5.32
Na_2O	0.00	1.33	0.60	0.44
SO_3	0.27	0.00	0.00	0.28
TiO_2	1.64	1.35	0.84	1.75
P_2O_5	1.22	0.31	0.23	0.62
Fe_2O_3	3.34	6.03	8.71	3.93

Table 3a – Clinker C4564 Compressive strengths (EN-196/1), MPa

Sample		1d str	%	2d str	%	28 str	%
FA C4672	blank	12.7		24.0		52.4	
FA C4672	TEA	13.7	7.9	23.9	-0.4	51.6	-1.5

FA C4672	TEA NaCl	14.7	15.7	25.4	5.8	49.6	-5.3
FA C4672	TEA NaSCN	16.0	26.0	26.5	10.4	51.6	-1.5
FA C4736	blank	13.1		23.0		53.3	
FA C4736	TEA	12.8	-2.3	23.8	3.5	53.7	0.8
FA C4736	TEA NaCl	15.0	14.5	24.8	7.8	51.4	-3.6
FA C4736	TEA NaSCN	15.9	21.4	25.1	9.1	50.8	-4.7
FA C4737	blank	11.9		22.2		47.9	
FA C4737	TEA	12.8	7.6	22.9	3.2	48.2	0.6
FA C4737	TEA NaCl	14.2	19.3	23.8	7.2	49.7	3.8
FA C4737	TEA NaSCN	14.5	21.8	24.3	9.5	48.7	1.7
FA C4738	blank	10.6		23.6		53.6	
FA C4738	TEA	13.4	26.4	25.3	7.2	56.8	6.0
FA C4738	TEA NaCl	15.0	41.5	26.4	11.9	54.4	1.5
FA C4738	TEA NaSCN	15.3	44.3	26.2	11.0	53.3	-0.6

Table 3b – Clinker C4705 Compressive strengths (EN-196/1), MPa

Sample		1d str	%	2d str	%	28 str	%
FA C4672	blank	13.4		23.2		49.5	
FA C4672	TEA	13.6	1.5	24.3	4.7	49.2	-0.6
FA C4672	TEA NaCl	15.1	12.7	24.0	3.4	48.7	-1.6
FA C4672	TEA NaSCN	16.2	20.9	24.8	6.9	50.6	2.2
FA C4736	blank	13.4		22.2		45.9	
FA C4736	TEA	14.3	6.7	23.4	5.4	45.2	-1.5
FA C4736	TEA NaCl	14.4	7.5	23.6	6.3	48.9	6.5
FA C4736	TEA NaSCN	15.4	14.9	23.8	7.2	48.0	4.6
FA C4737	blank	12.8		22.6		46.0	
FA C4737	TEA	13.7	7.0	22.9	1.3	48.0	4.3
FA C4737	TEA NaCl	14.4	12.5	22.8	0.9	46.8	1.7
FA C4737	TEA NaSCN	15.1	18.0	24.5	8.4	47.1	2.4
FA C4738	blank	13.9		22.7		50.6	
FA C4738	TEA	14.6	5.0	23.7	4.4	50.6	0.0
FA C4738	TEA NaCl	15.4	10.8	24.2	6.6	49.8	-1.6
FA C4738	TEA NaSCN	15.8	13.7	25.1	10.6	49.8	-1.6

4.Results discussion and analysis

The data analysis that follows focuses on the assessment of any correlation between compressive strength values and chemical composition of the fly ashes. Only the main fly ash components, namely alumina, silica and iron oxide, were considered at this stage. In addition, usual calculated parameters like Silica Ratio (SR) and Alumina Ratio (AR) were considered. Formulas used are the following:

Silica Ratio: SiO_2 / (Al_2O_3+Fe_2O_3)

Alumina Ratio: Al_2O_3/Fe_2O_3

SR and AR for this study were calculated only based on fly ash composition (i.e., not considering contribution of the OPC).

4.1 Clinker C4564

Strengths were plotted versus the chemical parameters and linear correlation equations were calculated. Graphs for each age and chemical parameter (along with the corresponding equations) are shown in Figures 1 to 4.

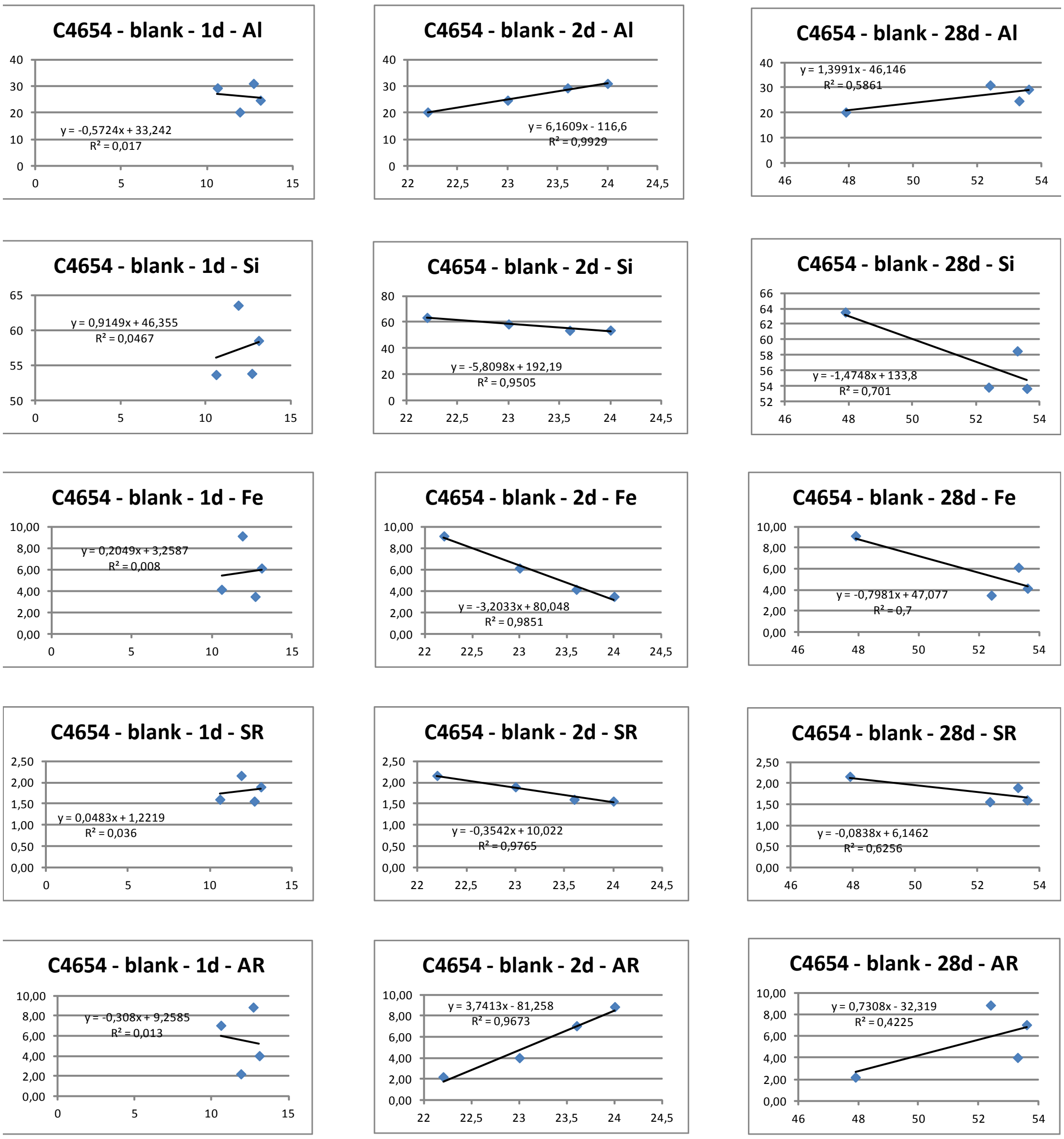

Figure 1 – Correlation between strength (MPa) and chemical composition of fly ashes (%) – Clinker C4654, blank

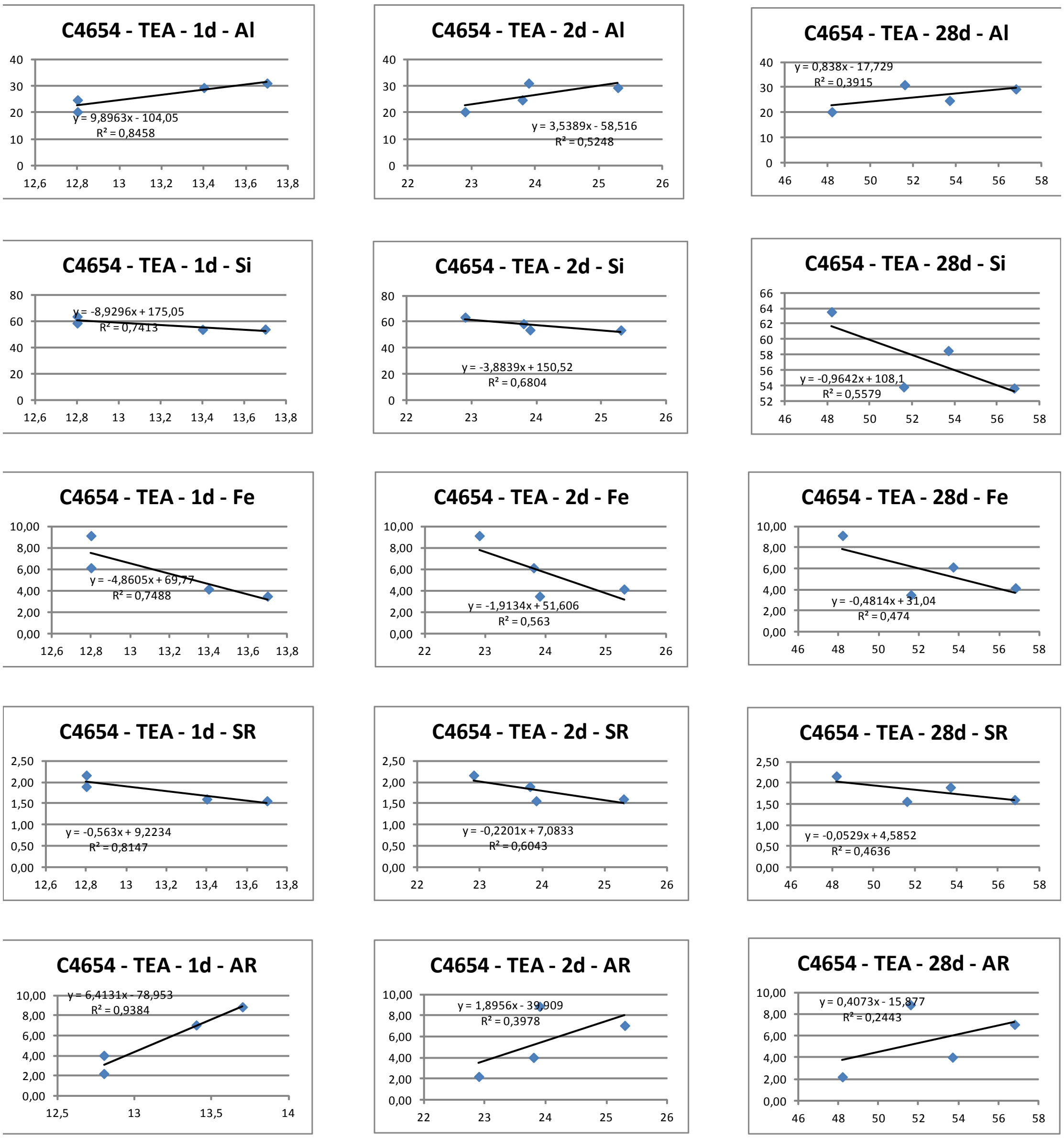

Figure 2 – Correlation between strength (MPa) and chemical composition of fly ashes (%) – Clinker C4654, TEA

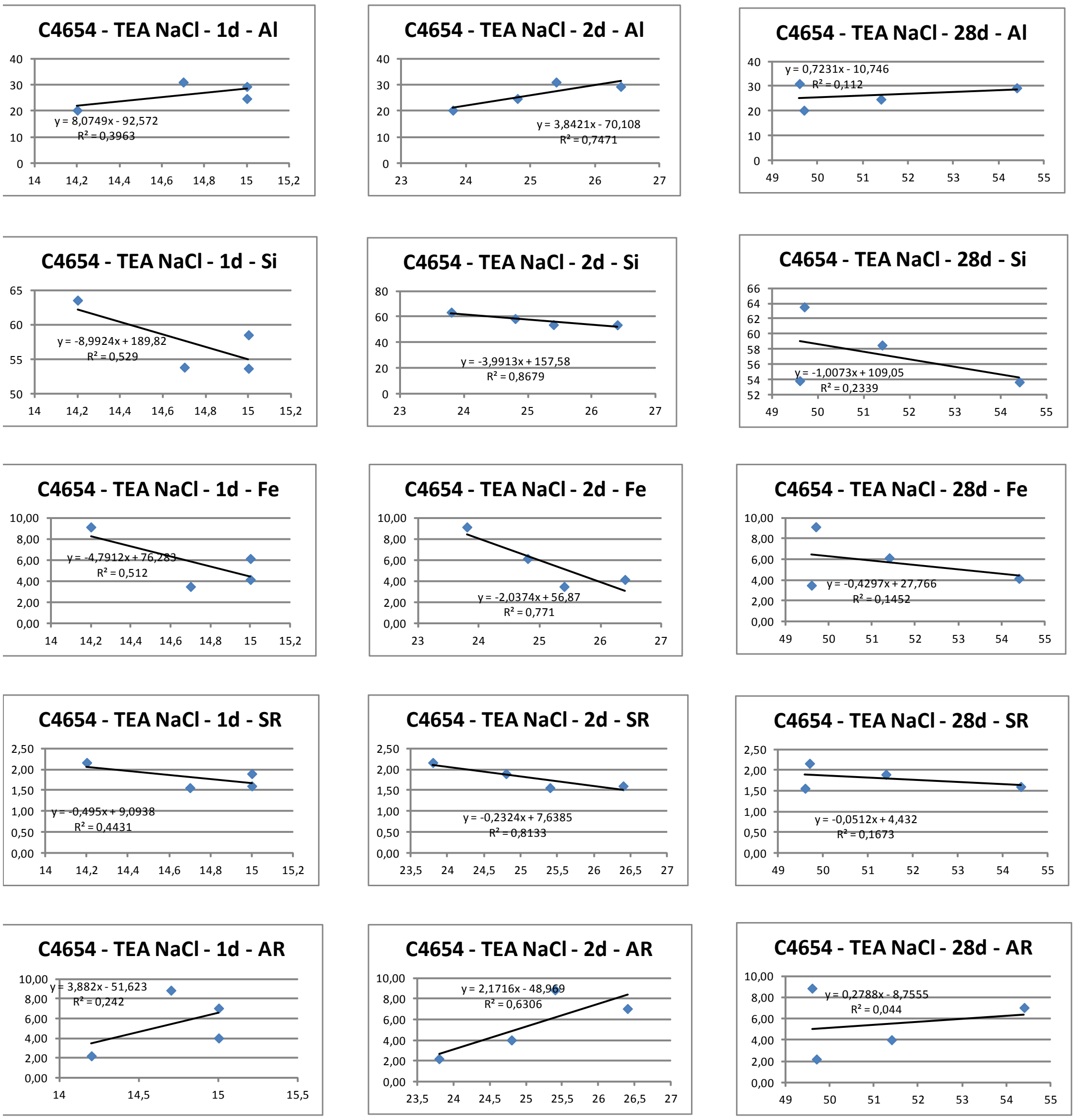

Figure 3 – Correlation between strength (MPa) and chemical composition of fly ashes (%) – Clinker C4654, TEA NaCl

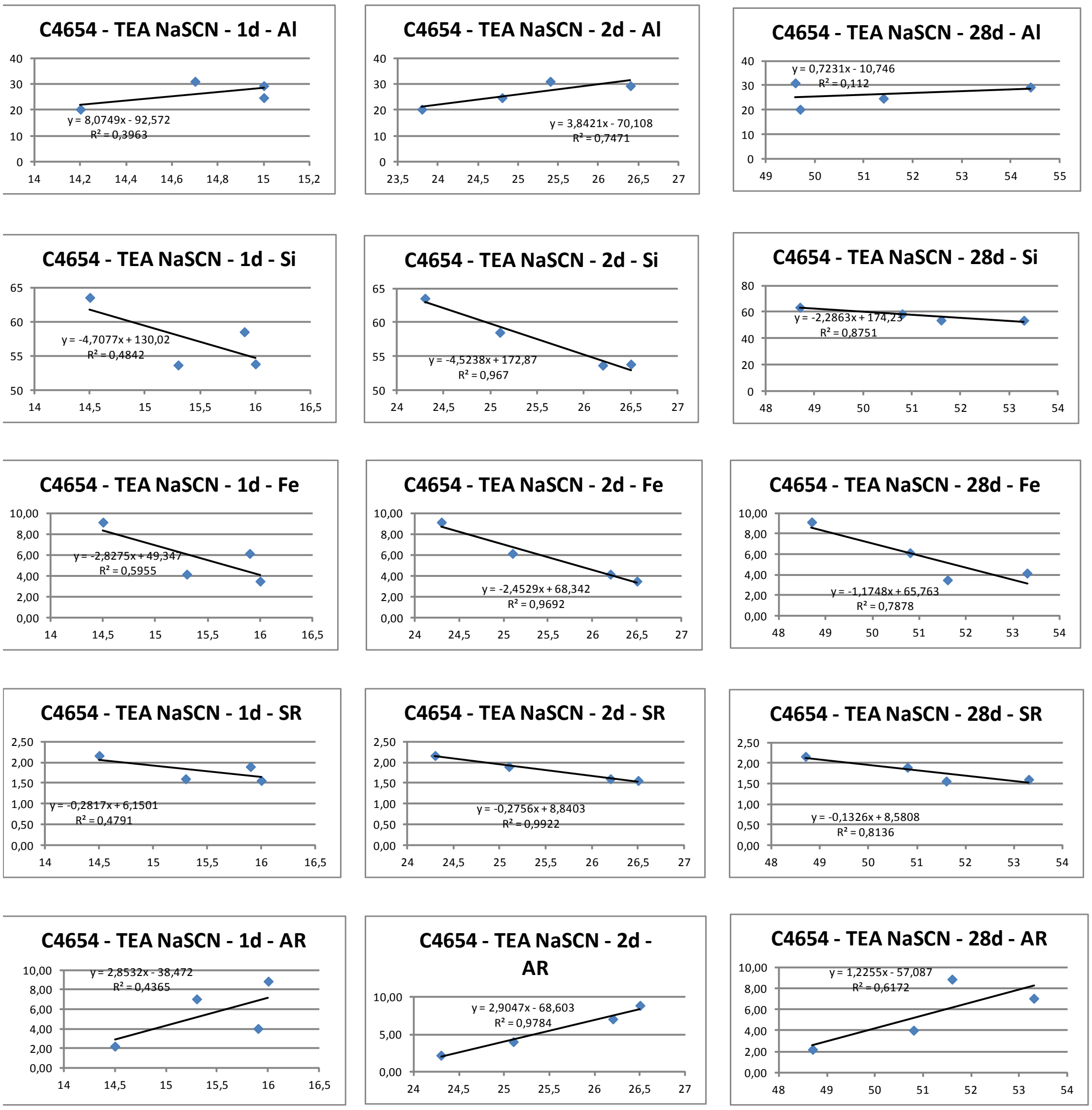

Figure 4 – Correlation between strength (MPa) and chemical composition of fly ashes (%) – Clinker C4654, TEA NaSCN

Table 4a reports R^2 linear correlation factor for the data referring to clinker C4564. Yellow color highlights strong correlations, while green is used for weaker, but still clearly visible, ones.

Table 4a – Clinker C4564 R^2 correlation factors

Age	Sample	Al	Si	Fe	SR	AR
1 day	blank	0.017	0.047	0.008	0.036	0.013
1 day	TEA	0.846	0.741	0.749	0.815	0.938
1 day	TEA NaCl	0.396	0.529	0.512	0.443	0.242
1 day	TEA NaSCN	0.511	0.484	0.596	0.479	0.436
2 days	blank	0.993	0.950	0.985	0.976	0.967
2 days	TEA	0.525	0.684	0.563	0.604	0.398
2 days	TEA NaCl	0.747	0.868	0.771	0.813	0.631
2 days	TEA NaSCN	0.996	0.967	0.969	0.992	0.978
28 days	blank	0.586	0.701	0.700	0.626	0.422

28 days	TEA	0.392	0.558	0.474	0.464	0.244
28 days	TEA NaCl	0.112	0.234	0.145	0.167	0.044
28 days	TEA NaSCN	0.748	0.875	0.788	0.814	0.617

4.1.1 Blank

For the cement prepared with this clinker, there is no correlation apparent at 24 hrs for the blank. At 2 days, strengths increase with higher Al content, and decrease with increasing Si and Fe. This is confirmed with SR (to which strength is inversely proportional) and AR (to which strength is directly proportional). At 28 days, correlation is definitely weaker, remaining visible in a more blurred way.

4.1.2 TEA

The addition of TEA, with the exception of fly ash C4736, gives a general early strength increase. 28 days effect is rather neutral.

In the presence of TEA, strengths develop a direct correlation at 1 day with Al content and AR; a weaker inverse correlation appears with Fe. Si by itself does not show a significant trend, but SR is inversely affecting strength on all spectrum.

4.1.3 TEA + NaCl

The addition of chlorides, while enhancing considerably early strength on all the samples, tends to cancel out any effect of the chemical composition of the ashes. Correlations showed by the blank almost disappear (they are discernable only at 2 days), and the ones generated by the use of the single addition of TEA are no more visible.

4.1.4 TEA + NaSCN

The different mechanism of action of thiocyanates (though not known) is evident through the fact that their correlation pattern is very different from the one showed by chlorides. A very strong strength increasing effect was recorded on all samples at 1 and 2 days. At 28 days this fades out or, in one case, a loss was found. Direct proportionality with Al content and AR is again evident at 2 and 28 days, as well as inverse proportionality to Si, Fe and SR, but not at 24 hrs, where the effectiveness of NaSCN is independent of these parameters.

4.2 Clinker C4705

Strengths were plotted versus the chemical parameters and linear correlation equations were calculated. Graphs for each age and chemical parameter (along with the corresponding equations) are shown in Figures 5 to 8.

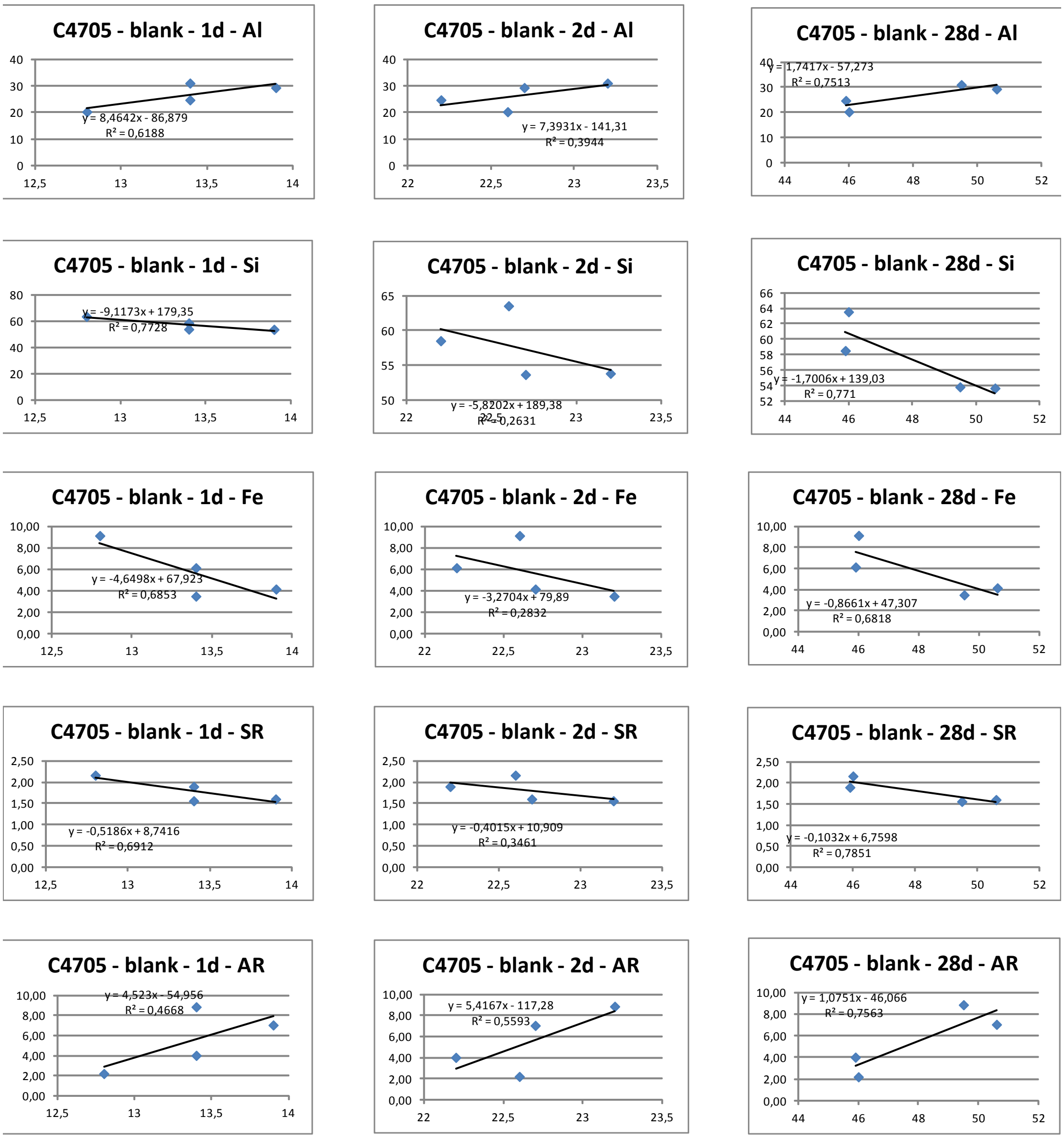

Figure 5 – Correlation between strength (MPa) and chemical composition of fly ashes (%) – Clinker C4705, blank

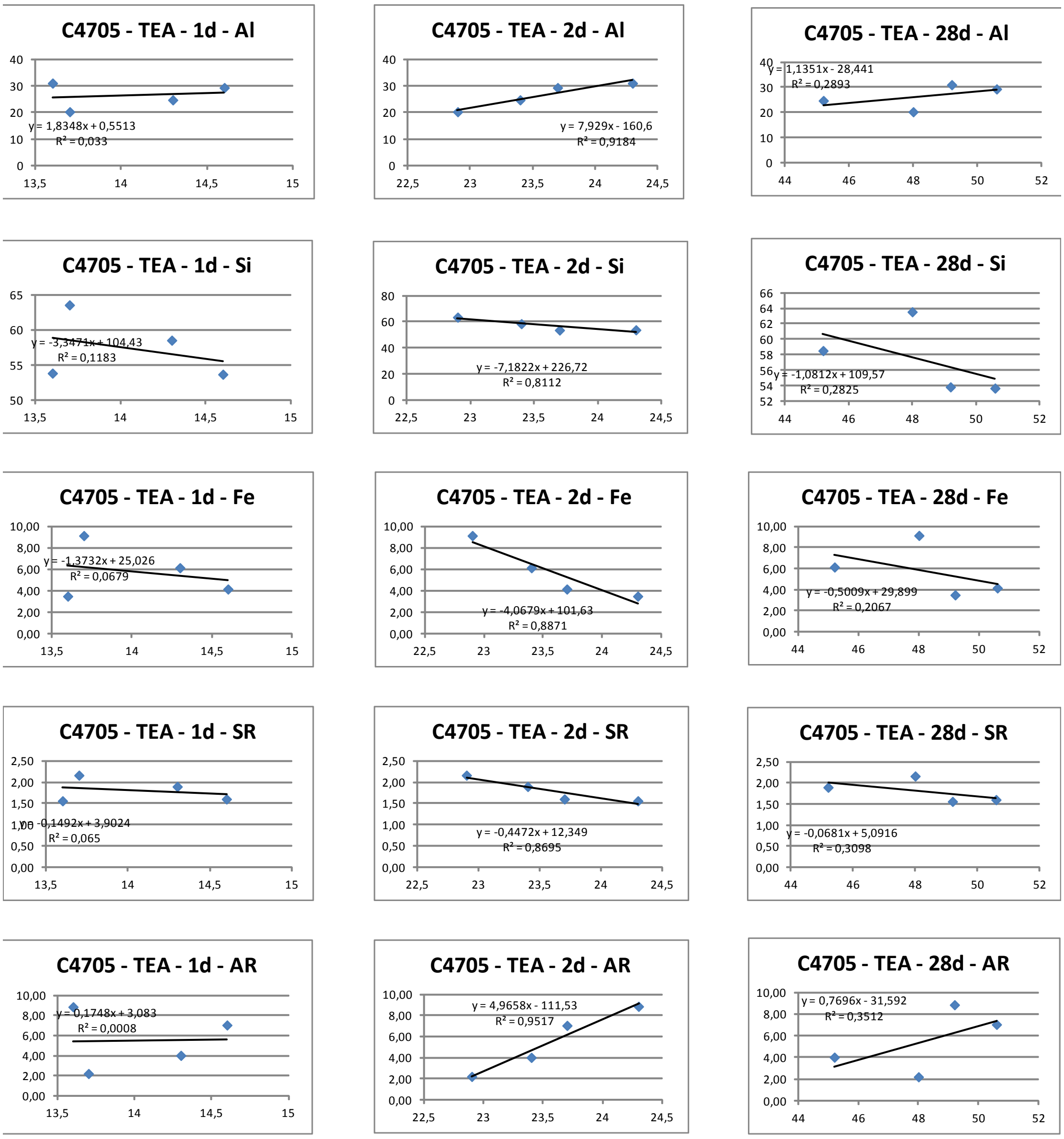

Figure 6 – Correlation between strength (MPa) and chemical composition of fly ashes (%) – Clinker C4705, TEA

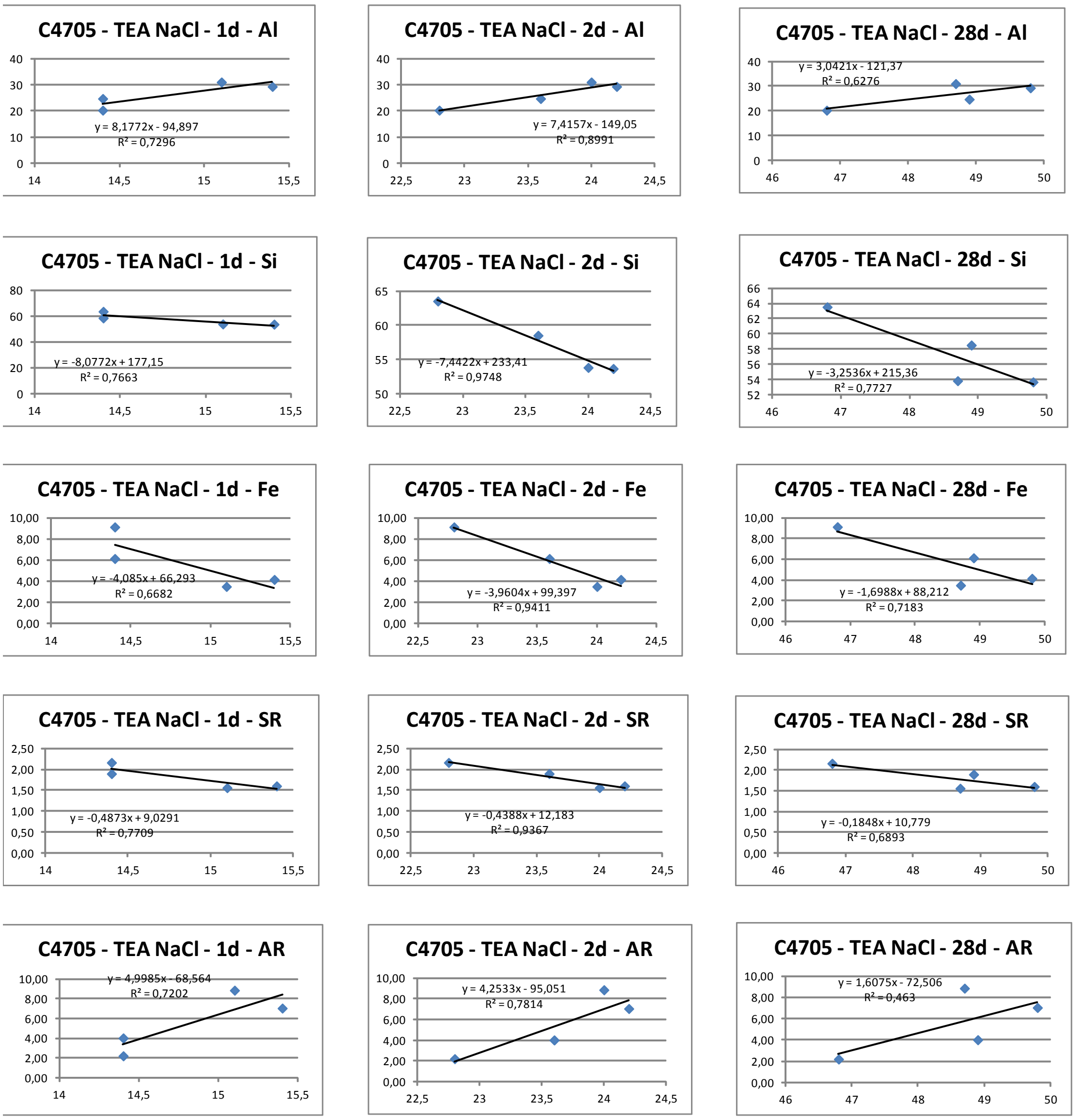

Figure 7 – Correlation between strength (MPa) and chemical composition of fly ashes (%) – Clinker C4705, TEA NaCl

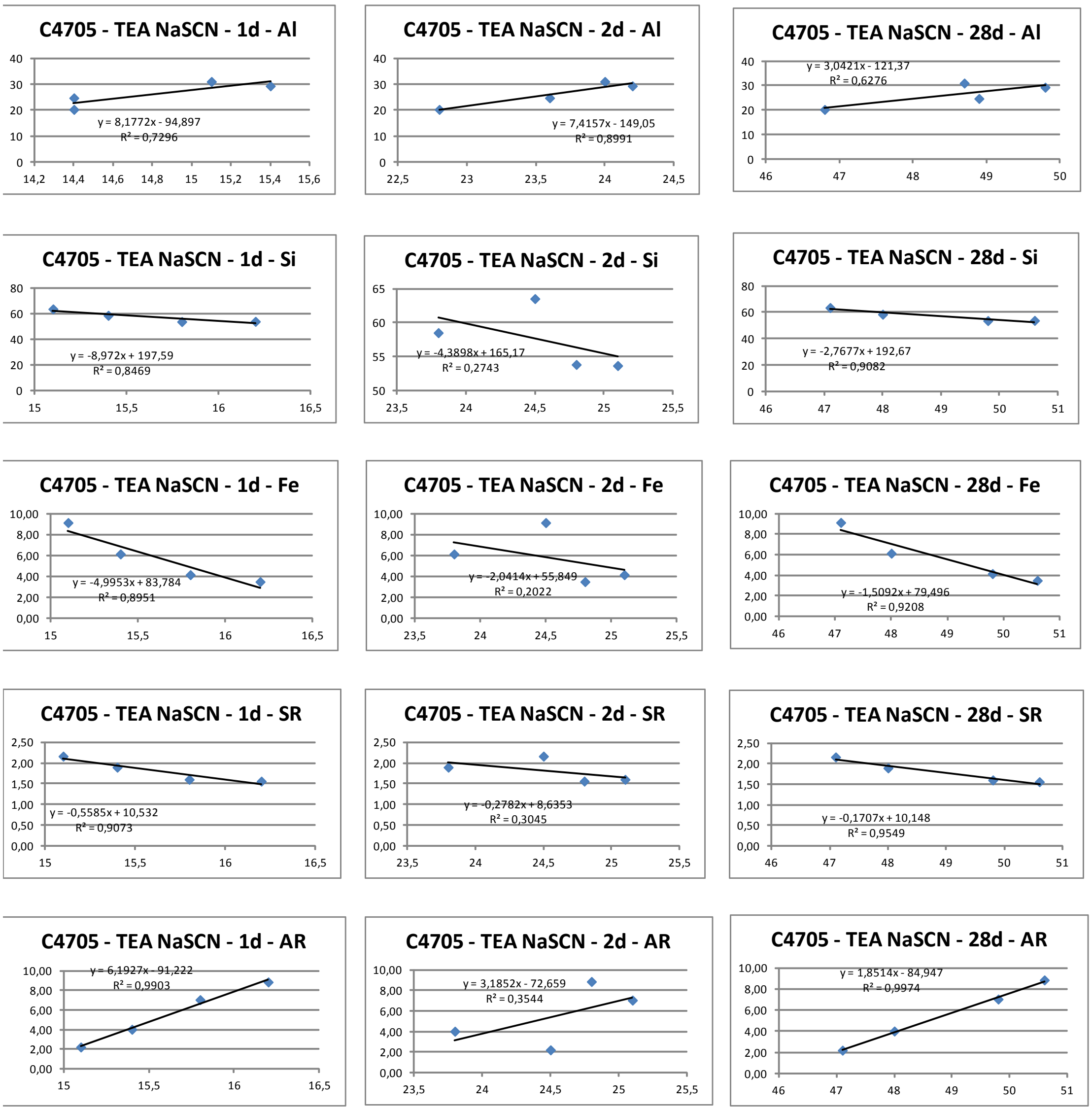

Figure 7 – Correlation between strength (MPa) and chemical composition of fly ashes (%) – Clinker C4705, TEA NaSCN

Table 4b reports R^2 linear correlation factor for the data referring to clinker C4705. Yellow color highlights strong correlations, while green is used for weaker, but still clearly visible, ones.

Table 4b – Clinker C4705 R^2 correlation factors

Age	Sample	Al	Si	Fe	SR	AR
1 day	blank	0.619	0.773	0.685	0.691	0.467
1 day	TEA	0.033	0.118	0.068	0.065	0.001
1 day	TEA NaCl	0.730	0.766	0.668	0.771	0.720
1 day	TEA NaSCN	0.946	0.847	0.895	0.907	0.990
2 days	blank	0.394	0.263	0.283	0.346	0.559
2 days	TEA	0.918	0.811	0.887	0.870	0.952
2 days	TEA NaCl	0.900	0.975	0.941	0.937	0.781
2 days	TEA NaSCN	0.287	0.274	0.202	0.304	0.354
28 days	blank	0.751	0.771	0.682	0.785	0.756

28 days	TEA	0.289	0.282	0.207	0.310	0.351
28 days	TEA NaCl	0.627	0.773	0.718	0.689	0.463
28 days	TEA NaSCN	0.973	0.908	0.921	0.955	0.997

4.2.1 Blank

In the case of clinker C4705, the most evident correlation is with Si content: at all ages strength decreases with higher Si %. Weaker, but discernible inverse (Fe and SR) and direct (Al) correlations are present, but not at 2 days.

4.2.2 TEA

TEA gives early strength increases and it's neutral at 28 days.

Compared to the blank, the reaction pattern changes with the addition of TEA: 24 hrs and 28 days lose any correlation, while at 2 days all the parameters show some proportionality: direct for Al and AR, inverse for Si, Fe and SR.

4.2.3 TEA + NaCl

Strong strength increase is shown at 24 hrs, less gain at 2 days, overly neutral at late ages.

With NaCl, all parameters show correlations, at all ages. Direct for Al and AR, inverse for Si, Fe and SR.

4.2.4 TEA + NaSCN

Strong to very strong strength increase is present at early ages, neutral effect at 28 days.

This is the case of stronger correlation for this clinker; very evident at 24 hrs and 28 days for all the parameters, but not recordable at 2 days.

4.3 Comments on the results

General considerations that can be made at this stage can be summarised as follows:

-the presence of a chemical additive changes not only the absolute strength of tested cement, but also its way of reaction, since correlation to the same chemical parameters varies greatly;

-though TEA was added in the same amount in all the addition tests, the presence of an inorganic salt changes again the picture very significantly, and the nature of such a salt plays a big role;

-in the average, higher the amount of Al in the fly ash, higher are the strengths of the cement; however, the presence of a chemical additive tends to flatten out this effect by enhancing the strength to a similar level;

-in the average, higher is the amount of Si in the fly ash, lower are the strengths of the cement. This correlation is relatively weak, though, and this effect is not normally seen as early as 24 hrs;

-in the average, higher is the amount of Fe in the fly ash, lower are the strengths of the cement. This correlation is rather weak;

-considerations above apply also to SR (inverse correlation) and AR (direct correlation);

-in the case of addition of TEA by itself, the most important correlation seems to be with Al, then with Fe, while Si content is not particularly related to the reactivity; this is in accordance with the studies that show the effectiveness of TEA as a complexant for Al and Fe;

-in the case of addition of TEA + NaCl, correlation pattern changes compared to TEA; it can be assumed that reaction mechanism should then be different;

-in the case of addition of TEA + NaSCN, correlation pattern is again different, and normally stronger for the parameters considered compared to both TEA and TEA + NaCl;

-based on the last two above considerations, addition of TEA + NaCl should be the less “sensitive” strength enhancing addition to increase early strength of a blended fly ash cement, in the sense that it can give a gain in strength irrespective of the chemical composition of fly ashes.

5.Conclusions

Additional work should be done on the subject to better understand the relation between chemical composition of fly ashes and their reactivity with chemical strength enhancers. At this stage, data collected can be a first step in better assessing the reaction mechanism of cement chemical additions, or at least in starting to build correlations between chemical parameters of blended cements and different additions.

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