ALKALIS AND CEMENT STRENGTHS

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ABSTRACT:

The effect of soluble alkalis on the strength development of two cements were evaluated in ISO-mortar and in two concrete compositions. Similar effects were found in all cases when tested on a constant w/c-basis.

The effect of soluble alkalis on the strength development of blended cements prepared by a partial replacement of a Portland cement by a granulated blast furnace slag, a fly ash and a microsilica was tested. No marked synergistic effects were found.

Key words: Strength, Alkalis, Concrete, Blended Cements.

1. INTRODUCTION

Though present in relatively small concentrations in Portland cement raw materials and clinker, the alkalis represent an important factor in the production of the cement as well as for the engineering properties of the final product. In the first case due to the high volatility of alkalis at the temperature level of clinker burning, and in the second case mainly due to their high solubility in water.

The tendency of alkalis to promote deleterious reactions with certain aggregates is undoubtedly the most important concrete technological aspect of alkalis in cement. However, for the cement producer the influence of alkalis on the strength development of cement is an important aspect as well. Hence, newer investigations /1,2,3/ have indicated, that variations in the content of water soluble alkalis is a dominant factor behind strength variations of modern industrial Portland cement clinker.

The general effect of an increased content of soluble alkalis is an increase in early strength and a decrease in late strength /1,2,3/. A similar effect on the degree of hydration of the clinker minerals has been demonstrated /4,5/ and though it has been indicated that the influence on strength can be explained by the changes in degree of hydration alone /6/, an influence through an impact on the quality of the hydration products formed cannot be excluded /7/.

The present paper concentrates on some practical aspects of the influence of alkalis on cement strengths. Firstly the relevance of results obtained in mortar tests will be considered and secondly some preliminary results regarding the influence of alkalis on the strength development of blended cements will be presented.

2. STRENGTH EFFECTS IN MORTAR AND CONCRETE

Cement strengths are commonly evaluated by a mortar test both in the quality control of cement production and in rearch work. So most of the experience on the effect of alkalis on cement strengths is in fact based on results of mortar tests.

However, Gebauer and Kristmann /2,3/ have in their investigation on industrial clinker tested the strength properties of the cements both in mortar and concrete. They found the positive effect of soluble alkalis in both the mortar and the concrete tests, while the negative effect on late strength was found only in the mortar test.

This result is rather puzzling if you assume that the effect of alkalis on strength is mainly to be traced back to their effect on the degree of hydration of the clinker minerals. From a practical point of view, the discrepancy referred to above is also important as it poses the question as to the relevance of mortar test to predetermine the behavior of cement in concrete.

To elucidate this problem further we have tested the influence of a K_2SO_4-addition on the behavior of two commercial cements in an ISO-mortar (3:1:0.5-mortar)/8/ and in two concrete compositions, a BS-concrete (3.5:2.5:1:0.6)/9/ and an internally used concrete composition of 3.3:3.0: 1:0.52. The two cements used were a normal Portland cement (Cement No. 1) and a special white cement with a low content of interstitial phase and alkalis (Cement No. 2). (Cement data in Table 2). The K_2SO_4 was added, dissolved in the mixing water, in an amount of 1.85% of the cement weight. This corresponds to an addition of 1.0% soluble K_2O.

The specimens were hardened 1 day in 99% RH at 20°C, then demoulded and subsequently hardened in water at 20°C.

To eliminate any influence of different air contents in the specimens, all strength data was corrected to zero air content by the expression $\sigma_o = \sigma \cdot \exp\left(5 \cdot \frac{a}{100}\right)$ where a is the air content determined by density measurements.

The strength results expressed as relative change of strength caused by the addition of K_2SO_4 (1% K_2O-sol.) is shown on fig. 1.

The expected effects - increased early strength and reduced late strength - are found for both cements in all three testing systems, and by using relative strength change the accordance between the test methods is fairly good, even in quantitative terms. The individual behavior of the two cements can easily be distinguished at least as far as early strength is concerned.

The effects illustrated in fig. 1 are based on materials having a fixed w/c-ratio. However, as the content of soluble alkalis can also influence the fresh concrete properties, additional experiments were performed where concrete strengths were compared on a constant slump basis (fig. 2). With the normal Portland cement the addition of alkali sulphate decreased workability and consequently increased the water demand to maintain the same workability (Table 1), which of course is followed by a decrease in strength at all ages.

The experimental results presented above indicate that the effects of alkalis on strength established in mortar tests are representative of what can be found in concrete at least when hardened in laboratory conditions. The effects demonstrated by the present experiments are based on an increase in soluble alkalis of 1% K_2O, which is about the maximum range observable in industrial clinker. An increase of this magnitude means a late strength decrease of 10-20%, which is 5 to 10 times the coefficient of variation of a well-performed strength test.

In practice the negative influence of a high alkali content on the late strength of a cement is primarily a problem of the cement producer, and in most cases it can be coped with by adjusting other parameters which influence the strength level e.g. the fineness of the cement.

TABLE 1

Fresh concrete data

		W/C	Slump (mm)	Vebe (sec.)
BS-concrete	Cement No. 1	0.60	80	2
		0.60	40	4
		0.64	80	2
	Cement No. 2	0.60	65	3
		0.60	65	3
FLS-concrete	Cement No. 1	0.52	25	6
		0.52	10	9
		0.535	25	7
	Cement No. 2	0.52	40	4
		0.52	45	3

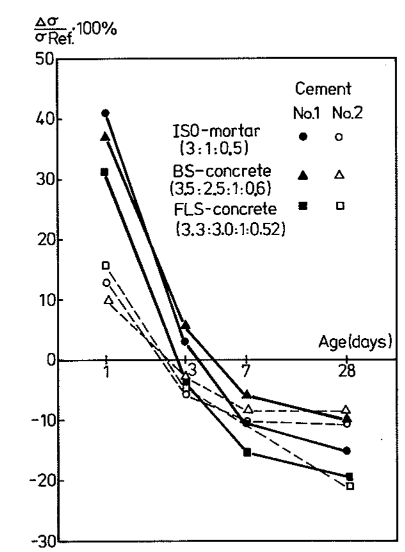


FIGURE 1: Relative change in strength of mortar and concrete by addition of 1.85% K_2SO_4 (1% K_2O-sol.) to the cement.

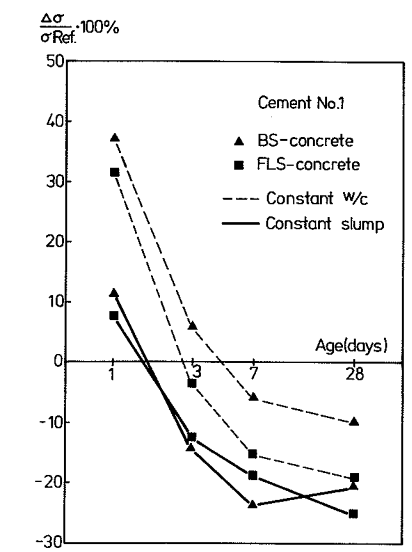


FIGURE 2: Relative change in strength of concrete by addition of 1.85% K_2SO_4 (1% K_2O-sol.) to the cement. Constant w/c and constant slump basis.

TABLE 2

Chemical and Physical data on materials used

	Cement No. 1	Cement No. 2	GBS	PFA	Micro-silica
SiO_2 %	21.9	24.4	32.3	45.35	96.7
Al_2O_3 %	6.31	1.60	12.2	30.51	0.61
Fe_2O_3 %	2.91	0.33	2.22	5.68	0.00
CaO %	61.1	69.3	43.2	7.29	0.16
MgO %	1.08	0.56	7.1	2.36	0.11
MnO %	0.05	0.02	0.22	0.07	0.01
TiO_2 %	0.33	0.09	0.45	1.48	0.04
P_2O_5 %	0.23	0.12	0.04	1.02	0.13
K_2O %	0.70	0.06	0.68	0.87	0.53
Na_2O %	0.33	0.17	0.24	0.46	0.14
SO_3 1) %	2.76	1.68	3.55	1.40	0.25
L.o.i.%	2.05	1.52	-1.20	1.28	1.53
K_2O-sol.%	0.34	0.02			
Na_2O-sol.%	0.08	0.03			
$\bar{\bar{K}}_s$ %	0.46	0.07			
Free CaO %	1.19	2.62			
Ins.res. %	3.64	0.18			
C_3S 3) %	52	70			
C_2S %	20	17			
C_3A %	10	4			
C_4AF %	8	1			
Spec.gravity	3.08	3.10	2.75	2.35	2.20
Spec.surface 4) $\frac{m^2}{kg}$	395	414	595	574	5930

1) Total sulphur content expressed as SO_3

2) $\bar{\bar{K}}_s = K_2O\text{-sol.} + 1.52 \cdot Na_2O\text{-sol.}$

3) Calculated potential composition (Bogue)

4) Blaine

3. STRENGTH EFFECTS IN BLENDED CEMENT

In mixtures of Portland cement with pozzolanic materials or granulated slags the Portland cement acts as an activator for the hydraulic reactions of these materials. An interesting question is to what extent differences in the content of alkalis in the Portland cement used in such mixes will influence the strength producing properties of the mixture as such. It is well known that the latent hydraulic reaction of granulated slag is activated by alkalis and that the impact of these increases with their concentration /10-11/. Correspondingly it is known that the solubility of silica increases with increasing alkalinity, a fact that might have a beneficial effect on the reactivity of pozzolanic materials.

So the negative effect of alkalis on the late strength development might be expected to be counteracted by a positive effect on the hydraulic reactions of intermixed hydraulic active mineral admixtures. To see the nature of effects on strength to be expected we have made some preliminary tests with blends of a Portland cement with a ground granulated blast furnace slag (GBS), a pulverized fuel ash (PFA) and a condensed silica fume (microsilica).

3.1 Materials and Procedure

As the basis cement for this experiment cement No. 2 was used which has a very low content of soluble alkalis (Table 2). Higher contents were simulated by adding K_2SO_4 to the mixing water in amounts corresponding to an augmentation of 0.5% and 1.0% K_2O. To eliminate a possible effect of the simultaneous increase in SO_3 when adding K_2SO_4, the SO_3 content of the cements was adjusted to the same value by adding gypsum as well. A survey of the tested modifications of the Portland cement is shown in Table 3.

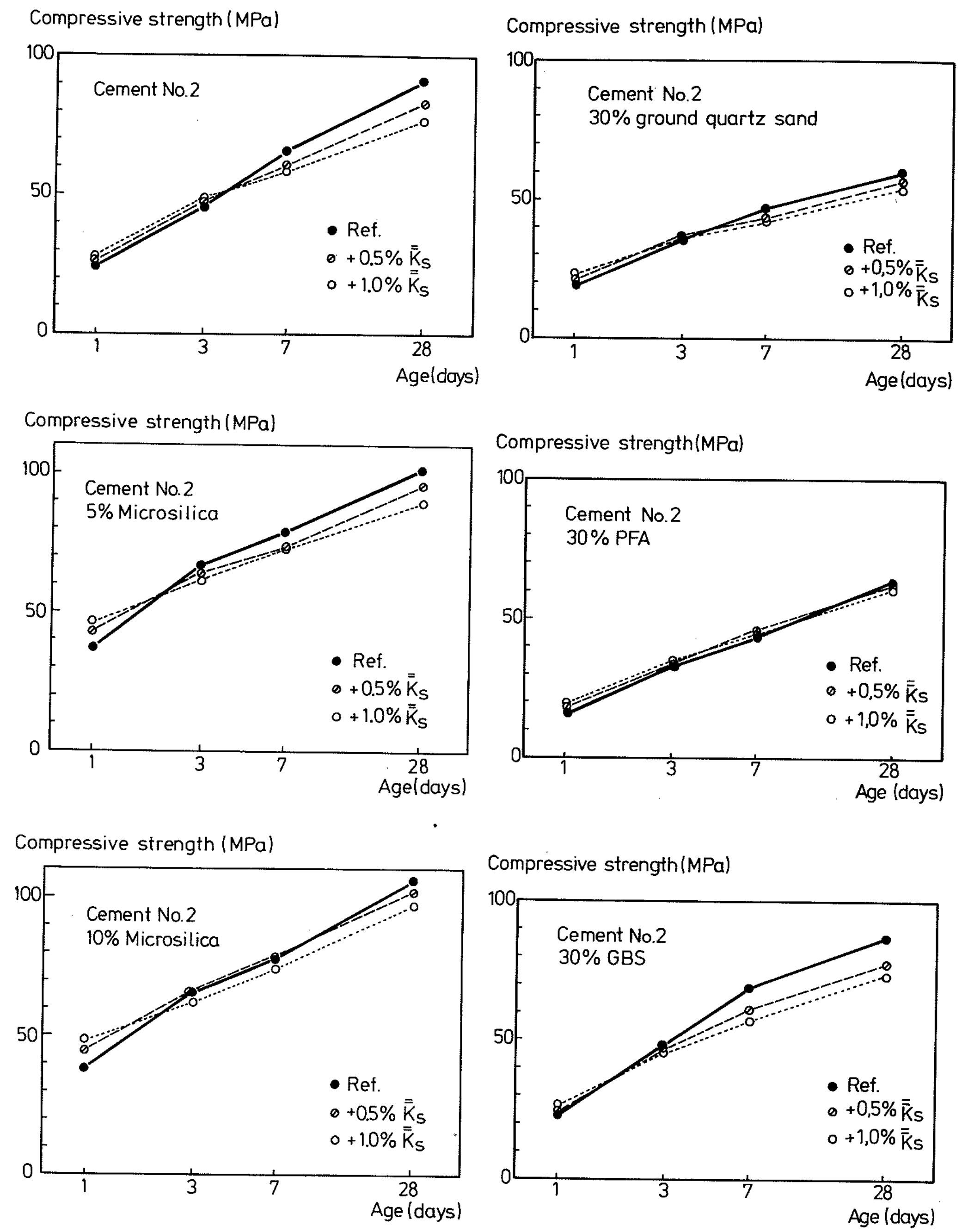
TABLE 3

Modifications of the Portland Cement

$\Delta\bar{\bar{K}}_s$ %	Additions		Augmentation in components	
	$CaSO_4 \cdot 2H_2O$ %	K_2SO_4 %	ΔSO_3 %	$\Delta(K_2O)_s$ %
0	1.85	0	0.85	0
0.5	0.925	0.925	0.85	0.5
1.0	0	1.85	0.85	1.0

Data on the materials used as partial cement replacements is given in Table 2. GBS and PFA were tested on a 30% replacement level and a reference test with the same amount of ground quartz sand was included. The PFA was used as received, the GBS and the sand were ground to a Blaine-fineness of about 600 m^2/kg, which brought the three materials on the same fineness level. Micro silica was added as received in amounts of 5 and 10%.

The strength development of the blends was tested in ISO-mortar (3:1:0.5) at 20°C. The modifying additions were added dissolved or dispersed in the mixing water, and the cement and the replacement material was blended directly in the mortar mixer. The strength was measured on smaller specimens than stipulated in the ISO-standard (1.9x1.9x14.4 cm prisms instead of 4x4x16 cm prisms). The strength results obtained with this specimens size are about 25% higher than those obtained with standard specimens.



FIGURES 3-8: Effect of content of soluble alkalis on the strength development of pure and blended cements.

3.2 Results

Fig. 3-8 show the strength development of the cements (all strengths corrected to zero air content in the mortar). The tendency of alkalis to increase early strength and decrease late strength is found in all cases. The change-over from positive to negative effect occurs after about 4 days in the pure Portland cement as well as in the quartz sand diluted cement. With 30% GBS the negative effect seems to occur at an earlier age and is apparently higher than with the corresponding quartz-sand diluted cement. With PFA the opposite tendency is indicated.

Cements with 5% and 10% microsilica give strength values well above the pure cement especially at early ages, irrespective of the alkali concentration.

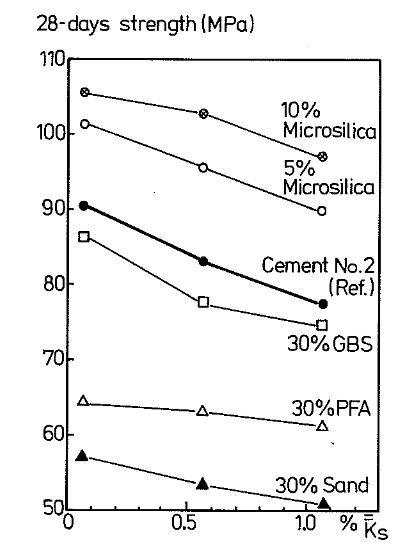


FIGURE 9: 28-days strengths of pure and blended cements as function of content of soluble alkalis in the Portland cement.

In fig. 9 the 28-days strengths of all the cements are plotted versus the content of soluble alkalis in the Portland cement. From this plot it is obvious that the main effect of the different mineral admixtures is the most dominant. The negative effect of increasing the amount of soluble alkalis is visible in all mixes. Interactions between the effect of the mineral admixtures and the alkali level of the Portland cement are indicated but are apparently small compared with the main effect of these.

The lack of any appreciable interactive effects indicated by these experiments is rather surprising and definitely calls for further investigations with other combinations of materials, other hardening conditions and a longer range of hardening limes before any general conclusions are drawn.

4. CONCLUSIONS

The potential of soluble alkalis to enhance early strength and diminish late strength of Portland cement has been demonstrated in ISO-mortar as well as in two concrete compositions. The strength changes expressed on a relative basis were of the same order of magnitude in these systems. The tendency of increased alkali contents to promote higher water demands can add an extra negative effect to the strengths at all ages if the effect of alkalis is evaluated on a constant slump basis.

Preliminary tests with blends of Portland cement with a granulated blast furnace slag, a fly ash and a microsilica have indicated that the influence on strength from such mineral admixtures is only modestly - if at all - dependent on the content of soluble alkalis on the cement.

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EXPERIENCES FROM THE USE OF F-CEMENT - A BINDER BASED ON ALKALI-ACTIVATED BLASTFURNACE SLAG

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1. ABSTRACTS

To meet the demands of the modern prefab. industry for a concrete giving high early and ultimate strengths a new binder, called F-cement, has been developed in Finland.
The cement consists mainly of a finely ground well granulated BFS used together with an admixture consisting of alkaline activators and a superplasticizer. The technical properties of the cement are very good and it can be used as an LH and SR cement.
The investment and production costs are low because no burning is needed.
The cement has been tested in full scale in ab. 40 prefab. factories in Finland and abroad. The first building made in F-concrete was erected last year in Rauma, Finland.

Keywords: Alkaliactivation, BFS, F-cement.

2. THE COMPOSITION OF F-CEMENT

The F-cement consists normally of 2 componets, namely a base-material and an admixture but can also be produced as a dry 1 component binder. As base-material is normally used a well granulated blastfurnace slag sometimes with addition of other metallurgical slags, natural or technical pozzolanes, PC or clinker etc. Fly ash addition up to 50% of the base-material weight has been used without detrimental effect on the strength. There is no special demands on the chemical composition on the BFS and slags even with low Al_2O_3-content have given base-materials with excellent strength properties.
The base-materials are activated by the F-admixture consisting of an alkaline solution of different salts and an effective usually lignosulphonate-based superplasticizer. The admixture is normally used as a solution with 25% dry material. The ratio of the admixture, used,calculated as dry, to the base-material is normally 4-7%.

3. PROPERTIES OF THE F-CEMENT AND -CONCRETE

Although the F-cement is based on by-products and wastes it is not to be looked at as a simple and cheap substitut for PC,but offers in many respects superior engineering properties compared to PC. The CaO/SiO_2 ratio of this binder is much lower than in PC and no free lime has been found in the hydration products. F-cement contains no C_3A and has thus excellent sulphate resistance properties. By the same cement content/m^3 the F-cement usually gives 20-30% higher compressive strength than OPC. The compressive strength being the same, the F-cement shows about 20% higher flexural strength.
Although the air content is low, usually only 1/2 - 1% the F-concrete is frost resistant. The shrinkage of the F-concrete is somewhat less than for corresponding PC-concrete, the creep about the same.