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S252

ALKALIS IN CLINKER : INFLUENCE ON CEMENT AND CONCRETE PROPERTIES

by Dr J Gebauer*

SYNOPSIS

The paper describes an investigation into the effects of the alkalis in clinker on the properties of cement and concrete. A large number of industrial clinkers have been studied by means of chemical analysis, X-ray diffraction analysis, light microscopy, scanning electron microscopy, microprobe and physical tests on cement, cement paste, mortar and concrete.

SAMEVATTING

Die referaat beskryf 'n ondersoek na die uitwerking van die alkalië in klinker op die eienskappe van sement en beton. 'n Groot getal nywerheidsklinker is ondersoek met behulp van chemiese ontleding, X-straaldiffraksie-ontleding, lig mikroskopie, aftaselektronmikroskopie, mikrosonde- en fisiese toetse op sement, sementbry, mortel en beton.

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1. INTRODUCTION

In the past five years, the Technical Centre *Holderbank* has taken a special interest in the relationship between clinker characteristics and the properties of cement and concrete. One of the reasons for initiating a study of this topic was developments in the manufacture and use of portland cement. The more sophisticated and demanding requirements for cement quality stipulated by users as well as changes in manufacturing technology have implied changes in the composition of cement. Among others, the large energy-saving production units with suspension preheaters employed today and the use of sulphur-rich fuel have lead to increases in the alkali and sulphate content of the clinker which is considered to have had the following negative side effects: poor storage stability of the cement; and premature stiffening and lower final strength of the concrete.

Our study was designed to critically examine these effects. Therefore, special attention was given to the alkalis and their influence upon cement and concrete properties. In the course of a comprehensive investigation, 57 different clinkers produced in 57 kilns at 48 different cement plants were collected. The clinkers and the cement, cement paste, mortar and concrete made from them were examined by means of chemical analysis, X-ray diffraction analysis (XRDA), light microscopy and physical tests. The ISO mortar test and a standardized concrete mix were used in the investigation. A selection of 11 clinkers out of the total of 57, each representing a group of several clinkers, were subjected to further special analytical procedures such as microprobe and scanning electron microscopy. Part of the results were presented and published[1] in 1978–79.

The various raw materials, fuels and processes applied in the production of clinker ensured a wide range of compositions representing a cross section of the portland cement clinker produced today. The ranges of clinker composition parameters are listed in Table 1.

TABLE 1: Ranges of clinker compositions (n =57)

	Minimum	Maximum	$\overline{x}$
C_3S %	36	69	54
C_2S %	8	43	23
C_3A %	1,0	13,4	8,5
C_4AF %	5,2	17,3	8,7
LS	85	101	93,5
SR	1,8	3,9	2,87
AR	0,7	3,1	1,88
K_2O %	0,04	1,40	0,41
Na_2O %	0,01	0,69	0,06
SO_3 %	0,04	1,30	0,54

I will confine my presentation to some of the essential findings of this study in regard to alkalis in clinker because a literature review will be given in another paper at this conference. The problem of alkali-aggregate reaction was not investigated in our study and will thus not be discussed.

2. DISTRIBUTION OF ALKALIS IN CLINKER

On the average, higher amounts of K_2O than Na_2O were recorded in clinker, whereby in the dry process an increased K_2O-content was ascertained compared to the wet process (see Table 2). The alkalis in clinker occur either as sulphates or in solid solution in clinker minerals.

TABLE 2: Alkali content in clinker according to kiln type

Kiln type		n	$\overline{x}$ (%) (average)	s (%) (std. deviation)
Na_2O	wet	25	0,26	0,13
	dry	21	0,24	0,18
	Lepol	11	0,24	0,10
	all kilns	57	0,25	0,14
K_2O	wet	25	0,49	0,31
	dry	21	0,73	0,29
	Lepol	11	0,76	0,30
	all kilns	57	0,63	0,32
SO_3	wet	25	0,43	0,31
	dry	21	0,70	0,31
	Lepol	11	0,46	0,35
	all kilns	57	0,54	0,34

(a) *Alkali sulphates.* Potassium sulphate, identified by XRDA as *arcanite*, constituted the predominant compound of alkalis in clinker. In some clinkers the double sulphate $3K_2SO_4 \cdot Na_2SO_4$, identified by XRDA as *glaserite*, was determined.

The total amount of potassium (sodium) sulphates in clinker estimated by means of XRDA and chemical analysis varied between 0–3,0 per cent.

Less frequently and in smaller quantities the calcium-potassium sulphate $2\,CaSO_4 \cdot K_2SO_4$ was present, identified by XRDA as calcium *langbeinite*. No pure calcium sulphate or sodium sulphate could be detected.

The soluble alkalis constitute an important and informative parameter for clinker composition. They were extracted from the clinker by dissolving them in cold water for 2 minutes. This method allows for the complete extraction of all alkalis present as sulphates. A more extensive extraction leads to the dissolution of some alkalis from the main phases, particularly the aluminates.

(b) *Alkalis in aluminate and ferrite.* The results of the chemical and microprobe analyses on the 11 selected clinkers are compiled in Table 3 which shows the distribution of alkalis and sulphates in the main clinker phases. Because of the semiquantitative character of the microprobe analysis, the quantitative values for the al-

TABLE 3a: Chemical composition of the selected clinkers

Clinker No.	Na_2O %	K_2O %	SO_3 %	Na_2O water soluble %	K_2O water soluble %	C_3S %	C_2S %	C_3A %	C_4AF %
1	0,11	0,39	0,29	0,03	0,16	65	17	7,7	7,6
2	0,15	0,50	0,28	0,02	0,13	62	19	8,0	7,6
3	0,05	0,63	0,60	0,03	0,49	52	25	9,4	7,9
4	0,12	1,30	1,11	0,12	1,00	45	29	13,4	5,5
5	0,42	0,61	0,39	0,08	0,35	57	21	8,0	8,5
6	0,18	0,70	0,35	0,04	0,38	57	22	2,7	4,3
7	0,45	0,80	0,64	0,12	0,58	62	16	11,8	5,5
8	0,32	0,82	0,95	0,16	0,70	63	15	11,3	5,5
9	0,04	0,08	0,18	0,01	0,01	67	16	2,4	10,9
10	0,11	1,10	0,84	0,08	0,91	56	21	8,8	8,5
11	0,06	0,15	0,43	0,01	0,03	45	32	10,4	7,0
$\overline{x}$	0,18	0,64	0,55	0,06	0,43	57	21	8,6	8,0
min.	0,04	0,08	0,18	0,01	0,01	45	15	2,4	5,5
max.	0,45	1,30	1,11	0,12	1,00	67	32	13,4	14,3

TABLE 3b: Average alkali and sulphate content in the main clinker phases of the selected clinkers

Clinker No.	In alite			In belite			In aluminate + ferrite		
	Na_2O %	K_2O %	SO_3 %	Na_2O %	K_2O %	SO_3 %	Na_2O %	K_2O %	SO_3 %
1	0,05	0,01	0,19	0,15	0,65	0,65	0,42	0,33	0,04
2	0,03	0,02	0,03	0,11	0,40	0,03	0,32	0,55	0,01
3	0,03	0,06	0,03	0,06	0,62	0,16	0,06	0,16	0,01
4	0,09	0,09	0,16	0,05	0,87	0,60	0,54	0,41	0,16
5	0,06	0,11	0,01	0,20	0,70	0,20	1,56	2,29	0,02
6	0,08	0,07	0,06	0,29	0,77	0,17	0,50	0,46	0,06
7	0,08	0,05	0,01	0,33	0,79	0,10	1,51	0,97	0,01
8	0,07	0,04	0,14	0,26	0,41	0,58	0,90	0,21	0,08
9	0,03	0,01	0,06	0,08	0,02	0,35	0,19	0,03	0,12
10	0,07	0,01	0,03	0,10	0,20	0,20	0,34	0,05	0,02
11	0,09	0,01	0,04	0,08	0,01	0,07	0,46	0,01	0,02
$\overline{x}$	0,06	0,04	0,07	0,16	0,49	0,28	0,62	0,50	0,05
min.	0,03	0,01	0,01	0,05	0,01	0,03	0,06	0,01	0,01
max.	0,09	0,11	0,14	0,33	0,87	0,65	1,50	2,29	0,16

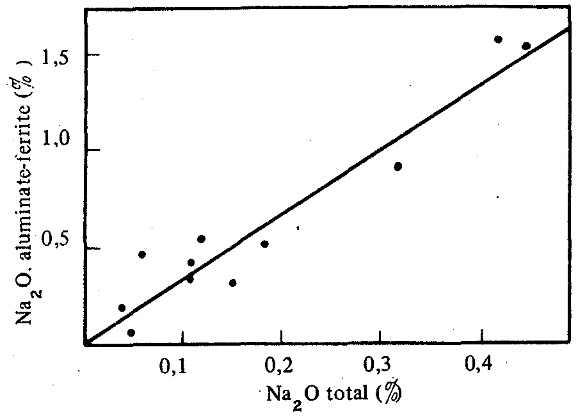

FIGURE 1: Relationship between the total Na_2O-content of clinker and the Na_2O-content of the aluminate-ferrite phase

kalis and sulphates in the main clinker phases should be considered as relative rather than absolute. They are intended to serve as a basis for the comparison of different clinkers.

As expected, on the average a significantly higher amount of sodium than potassium was incorporated into the aluminate-ferrite. A good correlation could be ascertained between the total Na_2O-content of clinker and the Na_2O-content in the aluminate-ferrite. Figure 1, in which the results of the microprobe analysis of the 11 clinkers are plotted, illustrates this relationship.

The alkalis are concentrated in the aluminate phase, particularly in the non-cubic alkali aluminate. Figure 2 illustrates the results of the microprobe analysis of clinker No. 7 showing the distribution of alkalis in the aluminate-ferrite phase as a function of the alumina ratio. The investigations have shown that a maximum of approximately 3,0 per cent Na_2O equivalent occurs in the alumina-rich part whereas only up to 1,0 per cent Na_2O equivalent is present in the iron-rich part of the aluminate-ferrite phase.

(c) *Alkalis in silicate.* On the average, the amount of potassium in belite was higher than that of sodium. The K_2O in belite is insoluble. The satisfactory correlation between the insoluble K_2O, calculated as K_2O total – K_2O

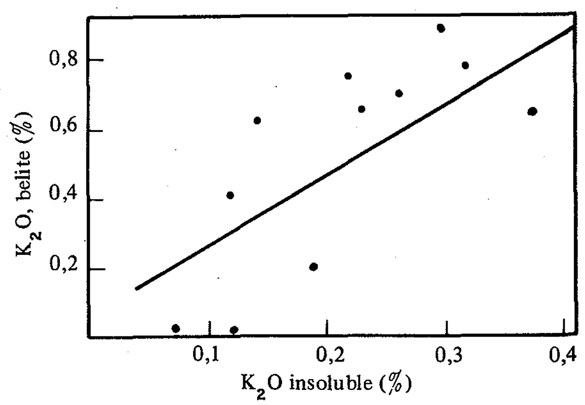

FIGURE 3: Relationship between the insoluble K_2O-content of clinker and the K_2O-content of belite

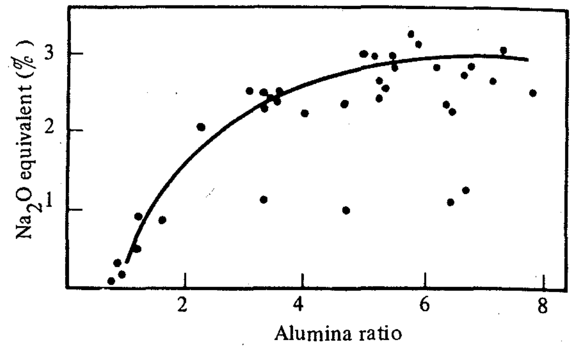

FIGURE 2: Relationship between alumina ratio and Na_2O equivalent of the aluminate-ferrite phase

soluble, and the K_2O in belite shown in Figure 3 confirms this statement.

The amount of alkali in alite is marginal; however, considering the high percentage of alite in clinker, a substantial amount of alkali may be incorporated into the alite.

We found a close correlation between the amount of alkali sulphate and particle size of alite: the higher the alkali sulphate content, the smaller the alite particle. The alkali sulphate may inhibit the crystal growth of alite as reported by Christensen and Johansen [2].

3. INFLUENCE OF ALKALIS UPON THE PROPERTIES OF CEMENT AND CONCRETE

(a) *Storage stability.* Poor storage stability caused by a high level of alkali sulphate in clinker was indicated by means of normal analytical methods and by scanning electron microscopy: alkali sulphate rich clinker having an alkali sulphate content of > 2,0 per cent easily forms needle shaped crystals of syngenite and ettringite upon exposure to humid air (see Figure 4). The cement made with these clinkers usually shows poor flow characteristics and a tendency toward lump formation when stored in silos and bags.

(b) *Properties of paste and ISO mortar.* The results of the statistical evaluation of the relationships between the clinker composition and the cement properties in standardized cement paste and mortar (ISO) are summarized in Table 4. For this investigation, the cement was prepared by grinding the 57 clinkers and a standard gypsum in a laboratory mill to a Blaine value of 3200 cm^2/g. The resulting cement samples were designated as standard cements as opposed to the industrial cements which were produced in the cement plant on an industrial scale and tested in another series of experiments.

Table 4 shows the correlations at the significance level of 1 per cent. From the values given it may be deduced, for example, that the C_3A increases the water requirement of the standard cement paste as well as shortening the setting time, thus increasing the 2-day strength and decreasing the 275 day strength of ISO mortar.

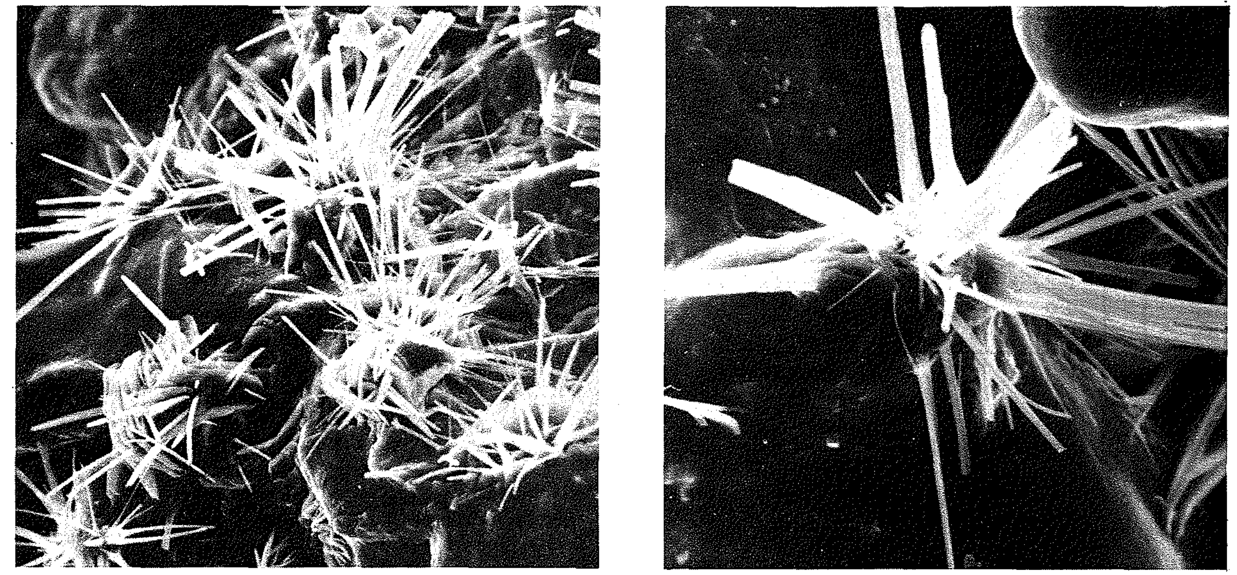

FIGURE 4: Syngenite and ettringite on clinker after 12 hours of exposure to humid air (x 2100) and (x 5400)

The study showed that the alkalis exert a rather small influence upon the properties of fresh cement paste. The best correlation existed between the alkali excess – expressed as the Na_2O equivalent not required for Na_2SO_4 and K_2SO_4 – and the water requirement of standard cement paste. Any attempt to further differentiate the type of alkali compounds and to find a significant influence upon the properties of fresh cement paste failed.

We came to the conclusion that the single most important parameter of the clinker composition influencing the ISO mortar strength is the *soluble potassium oxide.* Soluble K_2O, or K_2SO_4, considerably increases the 2 day and slightly decreases the 28 and 275 day strength of the ISO mortar. It is worth noting that at 28 and 275 days only the compressive strength is influenced by the clinker composition. The flexural strength of ISO mortar is not affected.

Our investigations gave some indication that the alkalis in the aluminate-ferrite phase or alkali excess impair the final strength of ISO mortar. This statement will have to be confirmed by additional investigations at present in progress.

TABLE 4: Correlation matrix, clinker composition and properties of standard cement (n = 57)

Chemical composition	Paste		ISO mortar compressive strength		
	Water requirement	Initial setting	2 days	28 days	275 days
C_3S	x	x	x	0,57	x
C_2S	x	x	x	–0,42	x
C_3A	0,65	–0,44	0,42	x	–0,43
C_4AF	x	0,34	–0,36	x	x
K_2O	0,42	x	0,67	–0,55	–0,69
Na_2O	x	x	x	x	–0,44
SO_3	x	0,34	0,71	–0,54	–0,49
K_2O sol.	0,33	x	0,81	–0,60	–0,64
Na_2O sol.	x	x	x	x	–0,44
Alk. sulphates	0,38	x	0,71	–0,54	–0,49
Na_2O equiv.	0,41	x	0,54	–0,60	–0,80
Na_2O excess	0,52	x	x	x	–0,38

TABLE 5: Regression models indicating the correlation between the composition of clinkers and the properties of standard cement.

			r (Correlation coefficient)
w. requirement (%)	=	$24{,}2 + 0{,}22\ C_3A + 1{,}7\ (K{+}N) - 1{,}5\ \overline{S}$	0,78
initial set (hr)	=	$4{,}13 + 0{,}17\ C_3A + 0{,}54\ \overline{S}$	0,59
S2 (N/mm^2)	=	$1{,}42 + 0{,}19\ C_3S + 0{,}35\ C_3A + 8{,}5\ K_{soluble}$	0,88
S28 (N/mm^2)	=	$40{,}3 + 0{,}28\ C_3S - 7{,}6\ K_{soluble}$	0,79
S275 (N/mm^2)	=	$76{,}0 - 11{,}4\ (K + N)$	0,82
$S\frac{2}{28} \times 100$	=	$2{,}1 + 0{,}3\ C_3S + 0{,}6\ C_3A + 10{,}4\ (K + N + \overline{S})$	0,89
$S\frac{2}{275} \times 100$	=	$-9{,}3 + 0{,}3\ C_3S + 0{,}8\ C_3A + 8{,}5\ (K + N + \overline{S})$	0,90

S = ISO mortar strength after 2, 28 or 275 days

$K = K_2O$ $N = Na_2O$ $\overline{S} = SO_3$

In addition to the correlation analysis between the clinker composition parameters and the cement properties, we have applied the technique of step by step multiple regression analysis using a large number of independent variables. In the following, I will present some examples of regression models indicating the correlation between the composition of the 57 clinkers and the properties of the standard cements (see Table 5 above).

The most significant correlations were obtained between the clinker composition and the rate of strength development expressed as the ratio of 2 to 28 or 2 to 275 day strength.

We have established similar regression models including also many other parameters such as for example the true mineralogical composition determined by means of XRD and microscopy instead of the Bogue's composition; type and particle size of clinker minerals; various minor components and types of alkali compounds. They also revealed significant relationships but did not considerably affect the conclusion that the alkalis, sulphates, C_3A and C_3S are the main parameters influencing cement properties, especially the ISO mortar strength. The evaluation of the various alkali types and their influence upon cement properties did not produce new aspects.

It is of advantage to use the overall chemical and Bogue's composition in the regression models as the necessary data are readily available in the cement plants.

However, I would like to emphasize that the information obtained by correlation analysis should be regarded with a certain degree of suspicion as the results, unless they are interpreted very carefully, may be misleading and there is a danger of abuse. First of all, trends rather than the quantitative part of the analysis should be considered.

There is also a danger of finding non-causal correlations since many of the variables show a high degree of interrelationship. For example, because of the relationship between alkalis and C_3A, the possibility of the alkali acting as a substitute for C_3A in the correlation analysis could not be precluded. In the study, we found that the alkalis may influence the microstructure of clinker, in particular the alite (see section 2(c)). Thus, it is possible that not the alkalis directly but the changed alite microstructure influences the cement properties; ie the alkalis may exert only an indirect influence.

The effect of alkalis on cement properties determined on the standard cements is more pronounced than that of the industrial cements. Thus, in the industrial cements (see Figure 5) for example, the correlation between the K_2O-content of clinker and the compressive strength of ISO mortar on the standard cements is diminished. This is explained by the fact that other significant parameters in the industrial cement, such as fineness of cement, gypsum quality and quantity, and possibly other additives to cement as well as their interaction with the clinker components play a decisive role and conceal the effect of a single parameter such as the potassium compounds.

(c) *Properties of concrete.* The above-mentioned relationship between the alkalis of clinker and the properties of cement in standard cement paste or mortar which are clearly evident in the standard cement and less pronounced in the industrial cements may only partially be inferred in the case of concrete. Attempts to find a correlation between alkali content and the properties of fresh concrete, in particular with regard to the water requirement and slump loss, have failed. Figure 6 shows the water requirement of concrete, expressed in terms of w/c ratio of the standardised concrete mix (300 kg cement per m^3 and slump = 75 mm) as a function of the alkali content in clinker and illustrates this fact. It is evident include the accuracy of proportioning (in particular the w/c ratio), the temperature of the concrete components, chemical admixtures, the curing conditions, and the dimensions of the specimen or concrete structure.

4. CONCLUSIONS

The influence of alkalis on the properties of cement, cement paste, mortar and concrete, which is quite apparent under standardized conditions but is less pronounced in industrially produced cement, may have completely disappeared in concrete produced under practical conditions.

The influence of alkalis on the properties of hardened concrete may still be recognized with regard to the early strength and the rate of strength development. Especially at early ages, the alkali concentration in the pore solution may play an important role in the hydration and hardening process.

The influence of alkalis on the properties of fresh concrete is marginal and it is probable that other influencing factors are predominant thus concealing the influence of the alkalis.

An isolated assessment of the alkalis with regard to cement or concrete properties may be misleading if other influencing parameters, their interrelations and their interactions are neglected.

Our study has demonstrated how complex the relationships are between clinker composition and cement properties. Frequently, published data generated by a single laboratory experiment which is performed on a small number of samples under particular test conditions may lead to false or exaggerated statements.

REFERENCES

1. GEBAUER J and KRISTMANN M *Influence of industrial clinker composition on cement and concrete properties.* 80th Annual Meeting of the American Ceramic Society, May 6 – 11, 1978, and World Cement Technology, March 1979.

2. CHRISTENSEN N H and JOHANSEN V *Mineralizers and fluxes in the clinkering process II. Kinetic effects on alite formation.* 7th International Congress on Chemistry of Cement, Paris 1980.

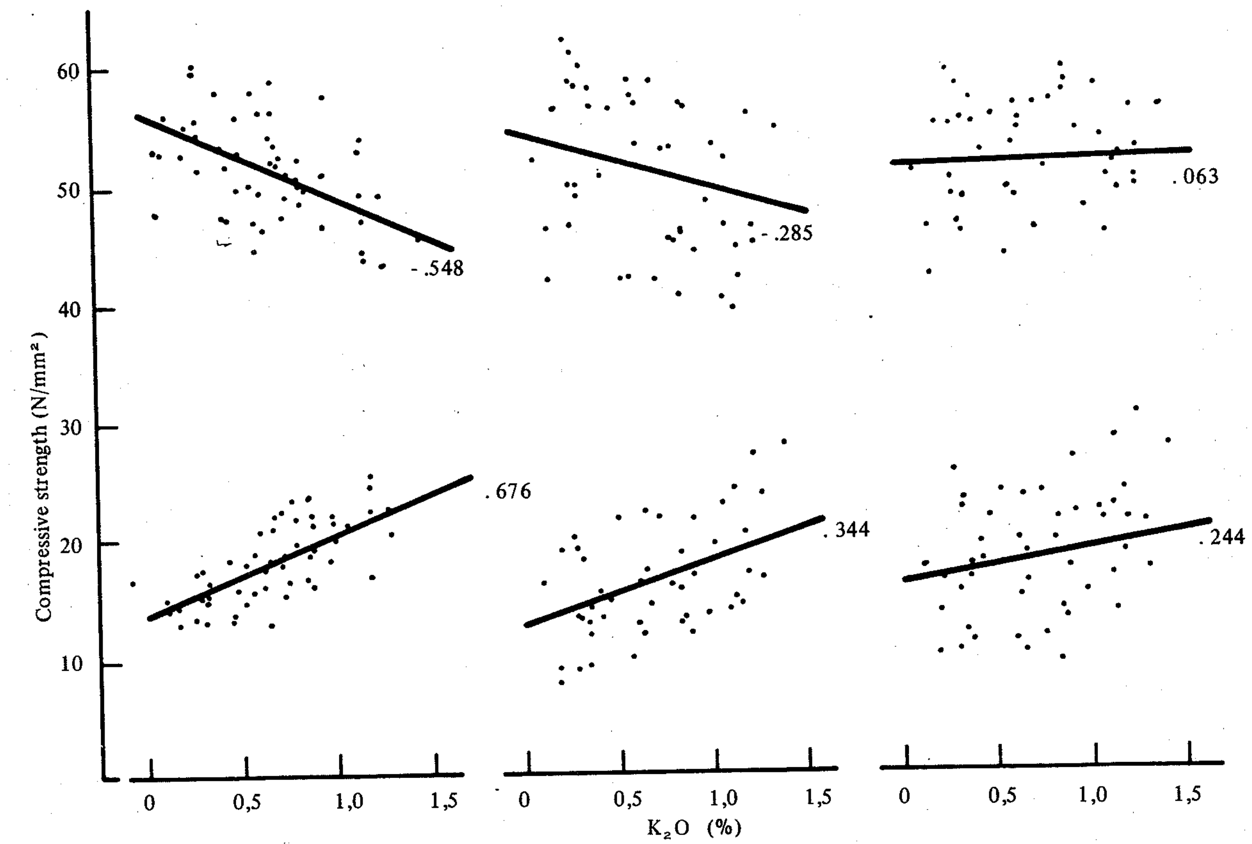

FIGURE 5: Compressive strength of mortar and concrete as a function of the K_2O-content of clinker

that this experiment performed on the 11 selected samples could establish no relationship.

Similarly, the diagram in Figure 7 showing the slump loss of standard concrete as a function of the alkali conent in the aluminate-ferrite phase indicates that the frequently claimed influence of alkali-aluminates upon the slump loss of concrete could not be confirmed.

A close relationship between alkalis and the properties of concrete was found only in so far as the early strength was concerned. The soluble K_2O, or even the alkalis in general, have a favourable effect upon the early strength of the standard concrete composition. On the other hand, no correlation could be ascertained between the alkalis and the 28 or 275 day strength of concrete.

The effect of alkalis on concrete properties is diminished by several other parameters and their interaction. In the standardised concrete composition, these interfering parameters may be the aggregates – sand in particular – having a diluting effect. In plant produced concrete, they may

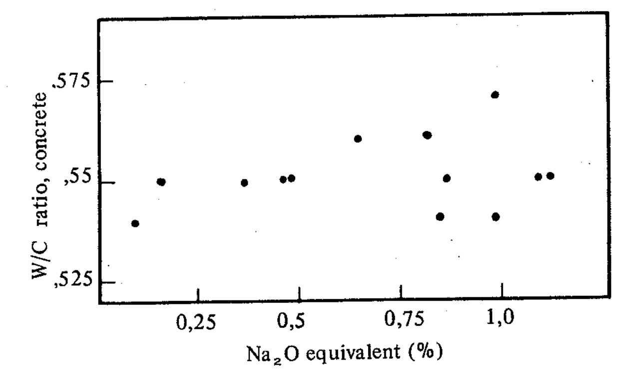

FIGURE 6: W/C ratio of concrete (slump 75 mm) as a function of total alkali content of clinker

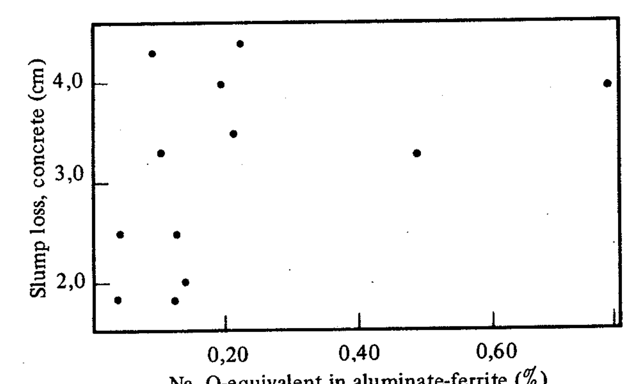

FIGURE 7: Slump loss of concrete after 45 minutes as a function of alkali content in the aluminate-ferrite phase

DISCUSSION

Dr P Grattan-Bellew (National Research Council, Canada) asked how sure Dr Gebauer had been that alkali sulphates were not present on the surfaces of the interstitial phases that he had analysed for alkalis.

Dr Gebauer replied that their analysis determined 10 elements simultaneously on each spot and that if, for example, aluminate had been analysed, they would have made sure that it was aluminate uncontaminated by sulphur. This was difficult to do, and places and spots were encountered where pure alkali sulphates were present, however such results had been excluded.

Dr J Skalny (Martin Marietta, Baltimore, USA) asked whether they had analysed by EDXA methods, and how accurate their measurements had been. He also inquired how the soluble alkalis had been determined.

Dr Gebauer said that they had analysed by EDXA methods using a whole range of standards and that this applied to the alkalis as well. He was of the opinion that the accuracy was almost as good as chemical analysis done by the X-ray fluorescence method. The soluble alkalis had been determined by extracting them for two minutes using distilled water.

ERRATA

The following corrections should be made in the body of Dr Gebauer's paper.

Page 1, column 1, Table 1: The figures for K_2O and Na_2O should read:

K_2O%	0,04 - 1,40	0,63
Na_2O%	0,01 - 0,69	0,25

Page 4, Table 4: The heading 'ISO mortar compressive strength' should also indicate that the figure is to 1% significance level.

Page 5, Table 5: The initial set regression Model should read '4,13 - 0,17 C_3A + 0,54 $\bar{S}$'.

Page 6, Figure 5: The bottom three curves are at 2 day strength while the top three are after 28 days.