Influence of Alkalies on the Strength Development

of Cements

Vagn Johansen

I INTRODUCTION

The use of modern economical dry process kiln systems has
resulted in an increase of the alkali content of PC clinker.
Further a desire to use relatively cheap high-sulphur fuels
in the cement industry, which is possible without excessive
SO_2 emission from the stack, will in many cases lead to a
higher SO_3 content in the clinker as well.

From a manufacturing point of view it implies that the level
of alkalies and sulphur in the clinker increases, when new
kilns are put into operation.

Experience has shown that the effect of this is a reduction
of the 28-day compressive strength, whereas the early strength
in most cases will increase.

As a consequence of this, many plants have observed a reduction
of the 28-day strength of more than 10% when old wet process
kilns are being replaced by dry process suspension preheater
kilns.

The alkalies in the clinker exist either in solid solution in
the clinker minerals or as sulphates.

In the literature it is apparent that much work has been
devoted to the examination of the effect of the alkalies in
solid solution on the hydration of the clinker minerals,
especially the aluminate phase. The literature dealing with
the effect of alkali sulphates is more scarce.

In the following I will show how the alkali sulphates in
clinker, and particularly K_2SO_4, are closely correlated with
the 28-day compressive strength.

Further, I will present results from recent experiments
(not yet completed), showing that addition of K_2SO_4 to a
cement has the same effect on the strength development as
the K_2SO_4 found in commercial clinker.

Finally, I will present some preliminary data concerning
the relation between the very early hydration and the strength
development of Portland cement.

II   DISTRIBUTION OF SULPHATE PHASES

In the following, the amount of K_2SO_4 always refers to the
clinker analysis.

It may be determined by direct extraction of the sulphates
with water, but it is a time-consuming and not always reliable
analysis.

We have developed a method according to which it is possible
to calculate the amount of potassium and sodium sulphate found
in the clinker. The method is based on the work of Pollitt [1]
and Brown, published in the Proceedings of the Tokyo Symposium,
1968. The best way of demonstrating it is by means of an
example.

The calculation is performed with the aid of two graphs;
Fig. 3 gives the fraction of the total alkalies to be found
in the sulphate phase as a function of SO_3/total alkali;
Fig. 2 gives the relative distribution of Potassium and Sodium
in the sulphate phase as a function of the K_2O/N_{K_2O} in clinker.

i   From the clinker analysis K_2O, Na_2O, SO_3, the sodium
        oxide is transformed to Potassium equivalents.

ii   Then the ratio of SO_3 to the total amounts of alkali
        oxides (in Potassium equivalents) is calculated.

iii   With these figures as abscissa Fig. 2 shows how much
        of the total alkalies is to be found in the sulphate
        phase.

iv   The amount of Potassium oxide relative to the amount of
      sodium oxide is calculated,

v   and from Fig. 2 the corresponding ratio in the sulphate
      phase will appear.

vi   Solution of the two equations gives the K_2O and Na_2O
      (as K-equivalents) in the sulphate phase.

III   ANALYSIS

On commercial clinker from 18 different plants and 33 different
kilns we have performed a multiple linear regression analysis
on the compressive strength as a function of the chemical
composition.[2] The clinker was ground to 3000 Blaine with
addition of 4% of gypsum (50% dihydrate and 50% hemihydrate).
The strength tests were performed according to the ISO Standards
(RILEM). Fig. 4 shows the variation of the chemical composition.

Fig. 5 demonstrates the 28-day strength as a function of
potassium sulphate only. When taking the C_3S into consideration,
the correlation is better, as shown in fig. 6. Variation of
the K_2SO_4 level by 0.3% gives a variation of 15 kg/cm^2 for the
28-day strength, corresponding quite well to the changes
experienced in practice.

The difference between the calculated and the measured 28-day
strength has a maximum value of 60 kg/cm^2, corresponding to
a coefficient of variation of 3%. This corresponds roughly
to the coefficient of variation of a Rilem strength test for
a single laboratory.

IV   LABORATORY EXPERIMENTS

In order to single out the effect of K_2SO_4, a series of strength
tests were performed on a grey cement and a white cement sample
with varying addition of K_2SO_4. Fig. 7 shows the composition of
the clinker.

The grey cement was obtained from a plant, the white cement was made in the laboratory from commercial white clinker.

The strength test was made on mortars according to the Rilem Standards, only the prisms were smaller (Mini-Rilem). By means of a conversion factor the compressive strength may be transformed to Rilem strengths.

Fig. 8 demonstrates the compressive strength for 1, 3, 7, and 28 days with varying additions of K_2SO_4.

The graphs clearly illustrate the increase of the early strengths and the decrease of the 28-day strengths.

This type of changes in the strength development is generally seen when the early strengths are accelerated in one way or another. A typical feature in these changes is that the 7-day strength remains almost unchanged, which is most clearly demonstrated by the grey cement.

Another way of illustrating the change in strength development is to plot the ratio of the 28-day strength to the 1-day strength versus the total K_2SO_4 content, as shown in Fig. 8.

For the white cement the ratio seems to level out at a certain content of K_2SO_4, meaning that the 1- and 28-day strengths are changed by the same factor.

In order to check the relationship between the strength and the content of K_2SO_4 and C_3S, we have converted the experimental 28-day strength from "Mini-Rilem" to Rilem, and then compared these experimental values with the values calculated according to the formula.

Fig. 9 shows the data, and it is seen that the agreement is really good. The formula predicts a decrease of 100 kg/cm^2 for a 2% increase in K_2SO_4, which is actually found. The better agreement is found for the grey cement. The data for the white cement shows a larger variation around the expected values, but not more than ~ 60 kg/cm^2.

From a practical point of view, the relationship between K_2SO_4 and the strength is very useful, and confirms many observations made. For instance, it is often said that "hard burning" is required in order to obtain good strength. By hard burning the evaporation of the alkalies and sulphur in the burning zone is increased, and, provided the volatile matter can escape from the kiln system, the content of K_2SO_4 in the clinker is reduced, which in turn gives a higher 28-day strength. Another observation is that addition of gypsum to the raw mix in some cases results in an increase of the early strength and a reduction of the late strength. This may be explained by the higher content of K_2SO_4 in the clinker due to the added sulphur.

V   EARLY HYDRATION

Besides the strength determinations the samples have been subjected to thermal analysis. Determination of the combined water shows for the 28-day samples that the strength is increasing with an increasing amount of combined water - as could be expected.

Examination of the pastes, of the same cements as above, hydrated for 3 minutes, shows that the amount of combined water (which is not bound to gypsum or in calcium hydroxide) has a negative correlation to the 28-day strengths.

Fig. 10 shows the strength plotted versus the combined water, which corresponds to "the corrected loss on ignition" in our previous work on prehydration of cement.

It is interesting that already after 3 minutes of hydration we can correlate the amount of chemically combined water to the 28-day strengths.
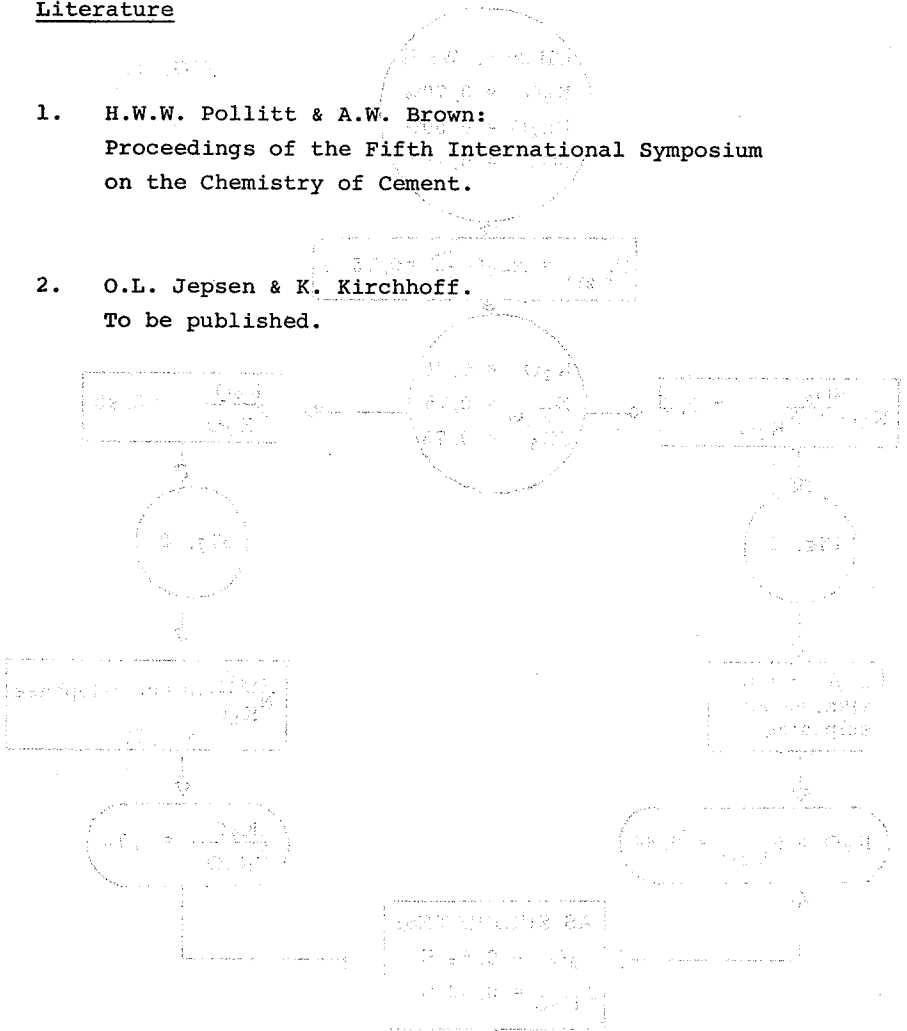
VI CONCLUSION

1. Summarizing our work it has been shown that the 28-day
    strength of cements may adequately be described by the
    K_2SO_4 and C_3S in the clinker. This relationship holds good
    when the clinker is ground to 3000 Blaine and with addition
    of 4% gypsum

2. Experiments with two different cements show that the effect
    of adding K_2SO_4 to these systems gives 28-day strengths
    which may be described by the same relationship as mentioned
    above.

3. The amount of combined water after 3 minutes of hydration
    of the cements mentioned correlates negatively to the 28-
    day strength.

    This seems to indicate that the reactions taking place in
    the very first period of time of contact between the cement
    particles and water is decisive for the strength develop-
    ment.

    Therefore, we will concentrate on these very early hydration
    processes also in relation to the physical properties of
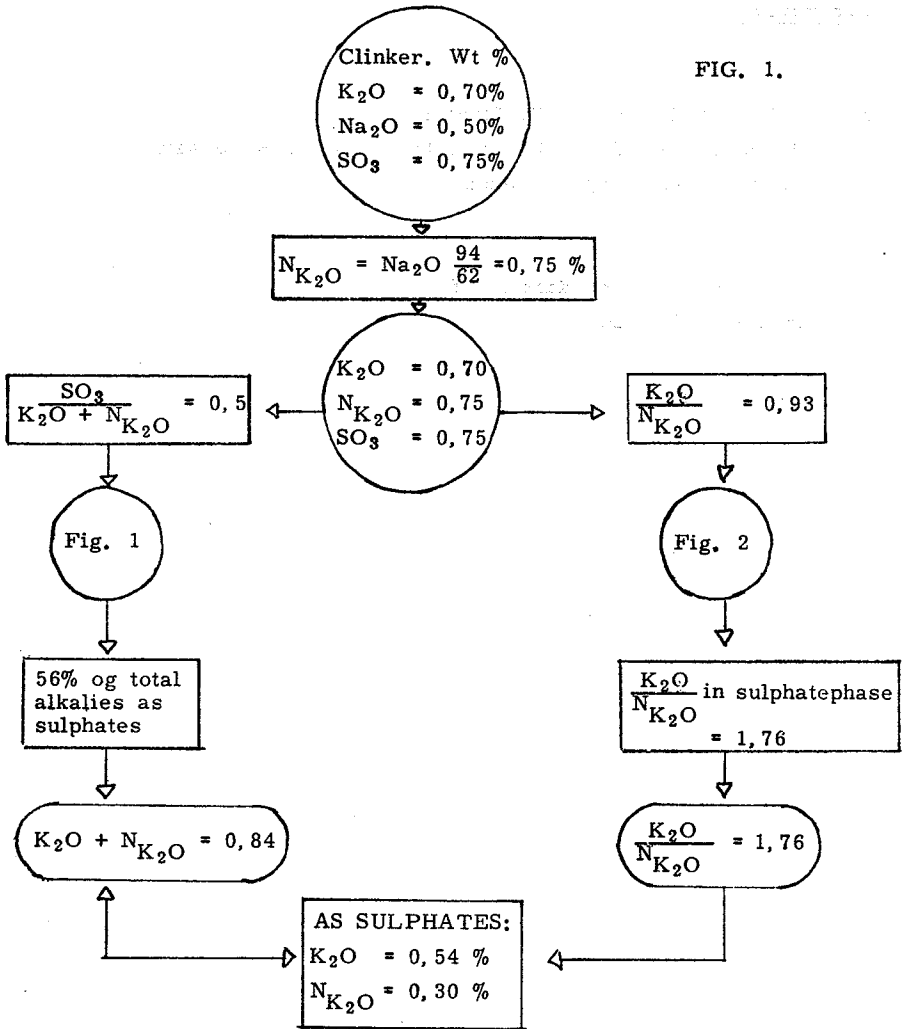   the cement particles and the reaction products.

Literature

1. H.W.W. Pollitt & A.W. Brown:
   Proceedings of the Fifth International Symposium
   on the Chemistry of Cement.

2. O.L. Jepsen & K. Kirchhoff.
   To be published.

FIG. 1.

Clinker. Wt %
$K_2O = 0,70\%$
$Na_2O = 0,50\%$
$SO_3 = 0,75\%$

$N_{K_2O} = Na_2O \frac{94}{62} = 0,75\ \%$

$K_2O = 0,70$
$N_{K_2O} = 0,75$
$SO_3 = 0,75$

$\dfrac{SO_3}{K_2O + N_{K_2O}} = 0,5$

$\dfrac{K_2O}{N_{K_2O}} = 0,93$

Fig. 1

Fig. 2

56% og total alkalies as sulphates

$\dfrac{K_2O}{N_{K_2O}}$ in sulphatephase $= 1,76$

$K_2O + N_{K_2O} = 0,84$

$\dfrac{K_2O}{N_{K_2O}} = 1,76$

AS SULPHATES:
$K_2O = 0,54\ \%$
$N_{K_2O} = 0,30\ \%$

	Total Wt %	As Sulphates	
K_2O	0,70 %	0,54 %	0,99 % K_2SO_4
Na_2O	0,50 %	0,19 %	0,55 % Na_2SO_4
SO_3	0,75 %	0,71 %	
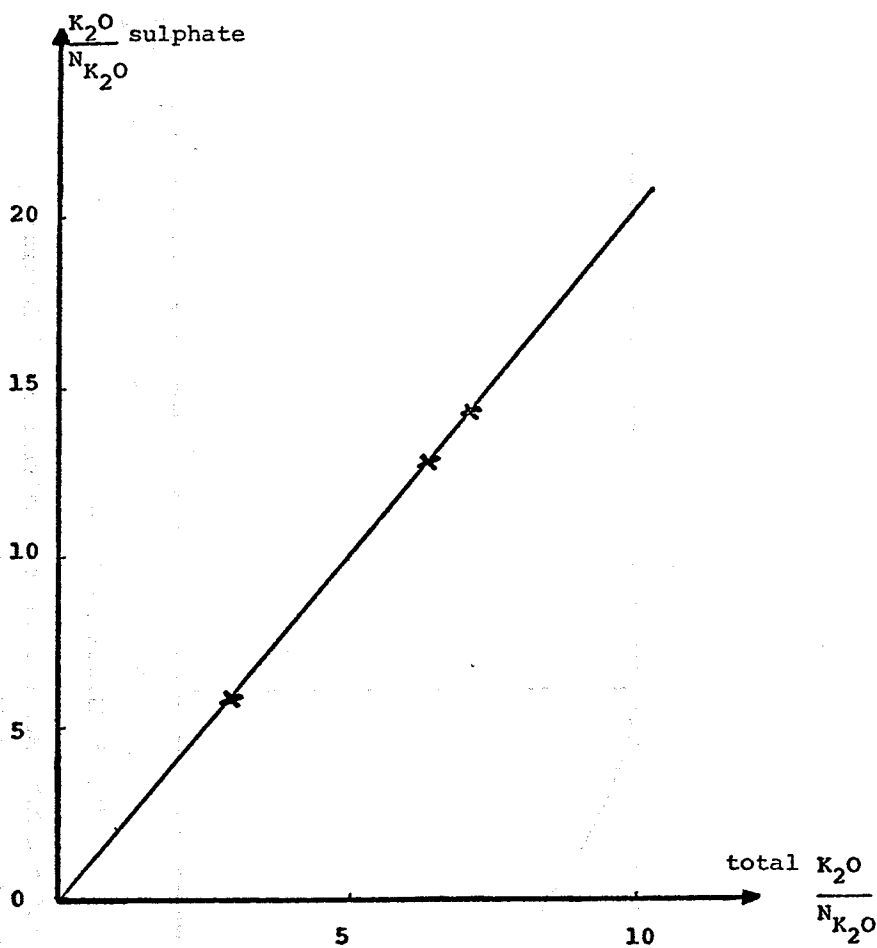
Fig. 2. : Na-K - distribution
in clinker.

Data from H.W.W. Pollitt & A.W. Brown.
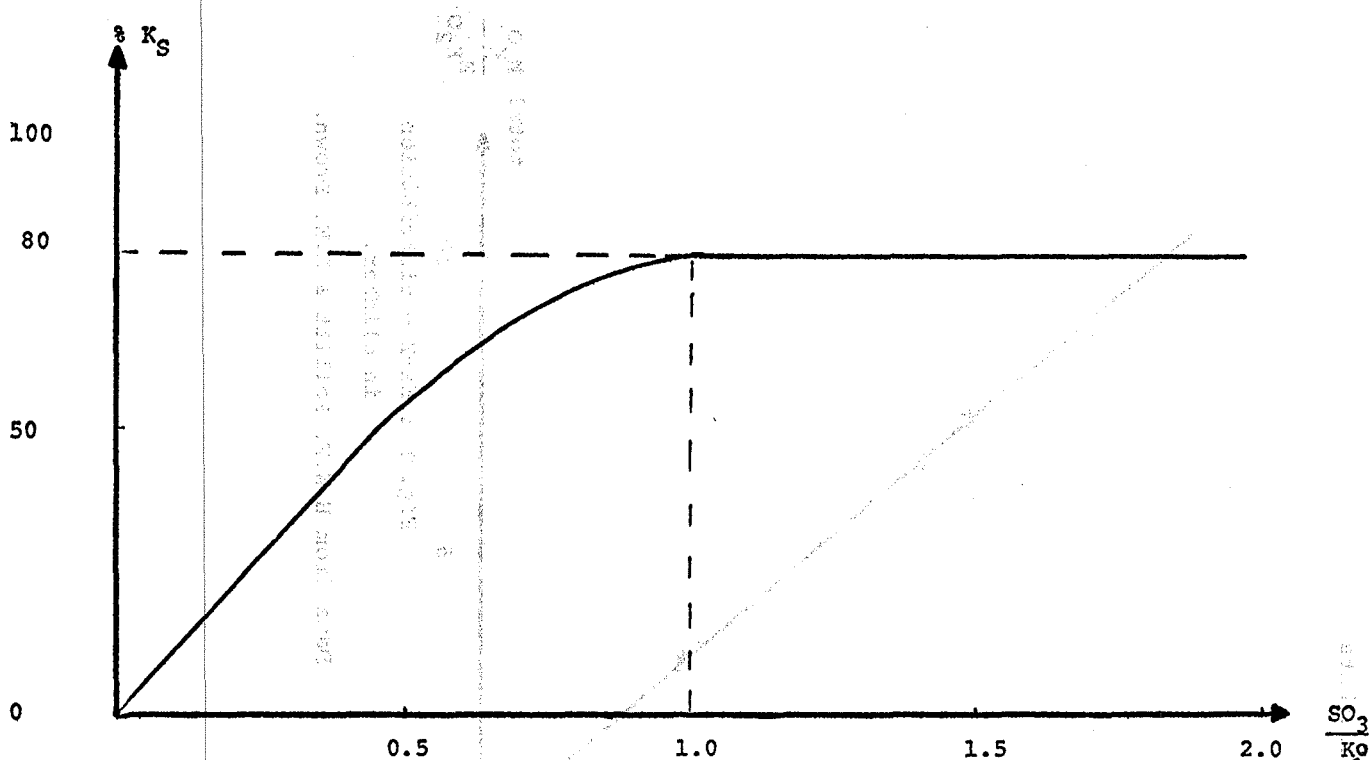
Fig. 3 Alkali as Sulphate

Data from H.W.W. Pollitt & A.W. Brown based on analysis of 10 laboratory clinker and 30 commercial from 20 different plants.

FIG. 4.

C$_3$S	44	- 77 %
LSF	88	- 99 %
SM	2, 4	- 5, 8
AM	0, 9	- 3, 5
K$_2$O	0, 1	- 1, 5 %
Na$_2$O	0, 1	- 0, 75 %
SO$_3$	0, 1	- 2, 2 %

FIG. 5

S28 = F (K2SO4)

S28-KG/CM2

600.0   550.0   500.0   450.0

.50   1.00   1.50   2.00

% K2SO4

92

FIG. 6

S28=420-50K2SO4+2. 5C3S

28D-CALC

28D-EXP/100.
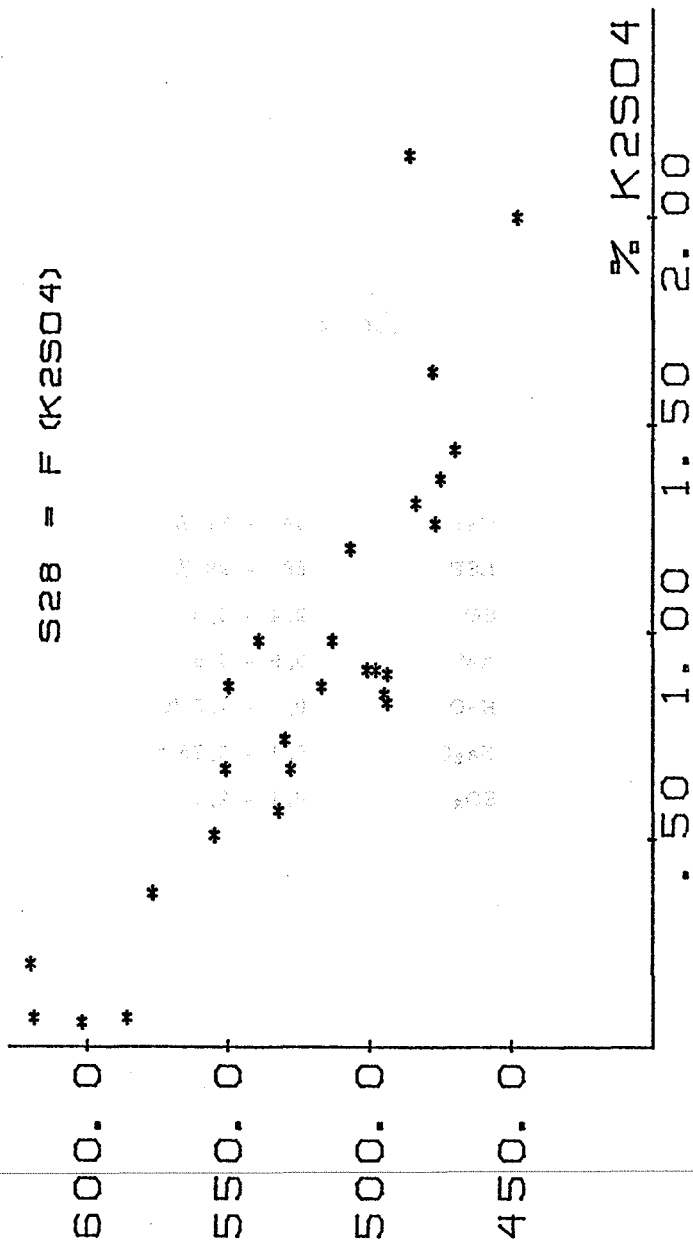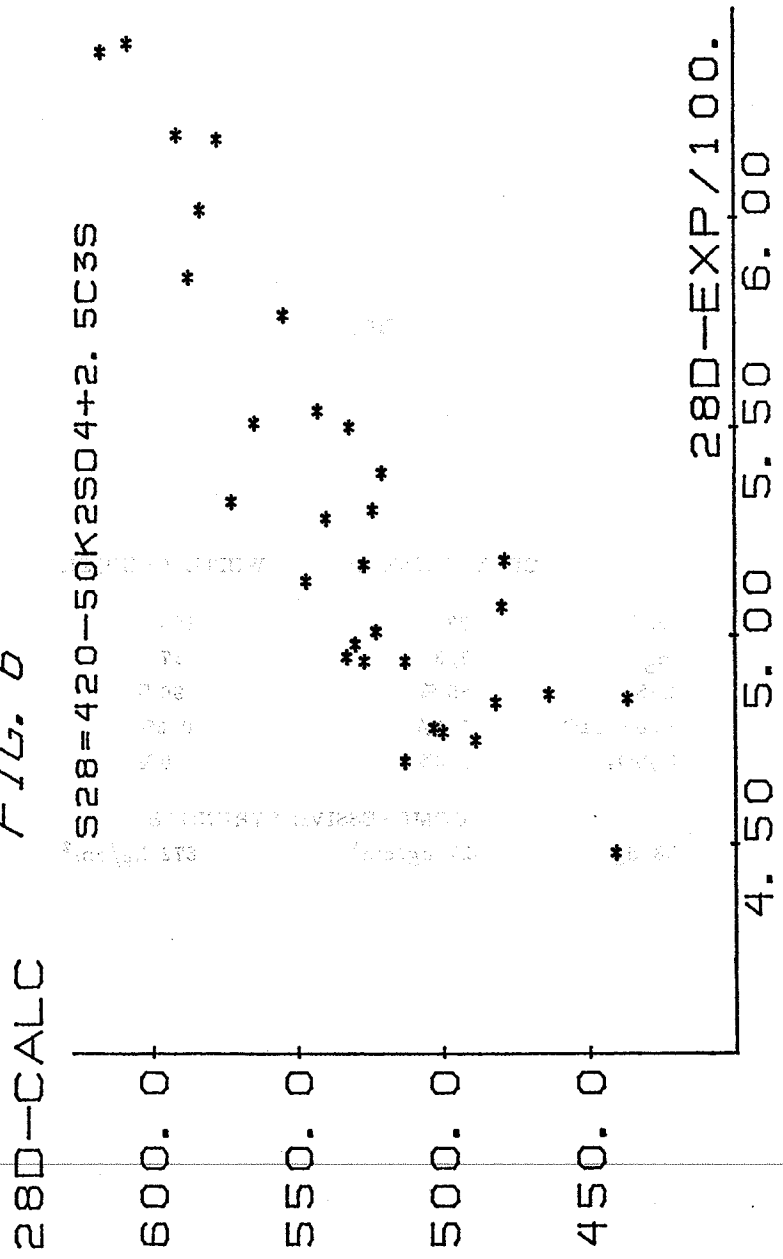
FIG. 7

	GREY CLINKER	WHITE CLINKER
LSF	93	100
M_S	2, 3	17
C_3S	55 %	90 %
Free CaO	0, 6%	0, 6%
K_2SO_4	1, 0%	0 %

COMPRESSIVE STRENGTH

28 dg	527 kg/cm^2	672 kg/cm^2
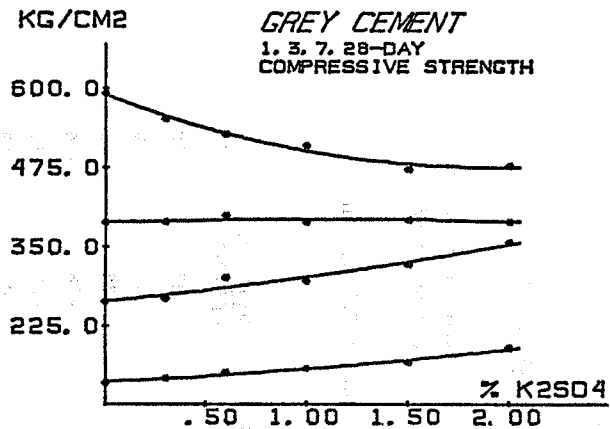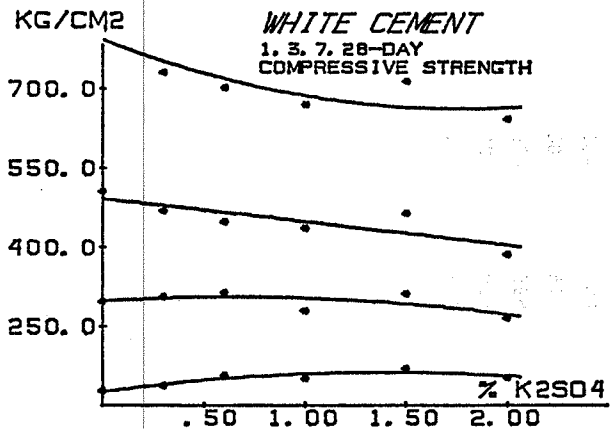
Fig. 8
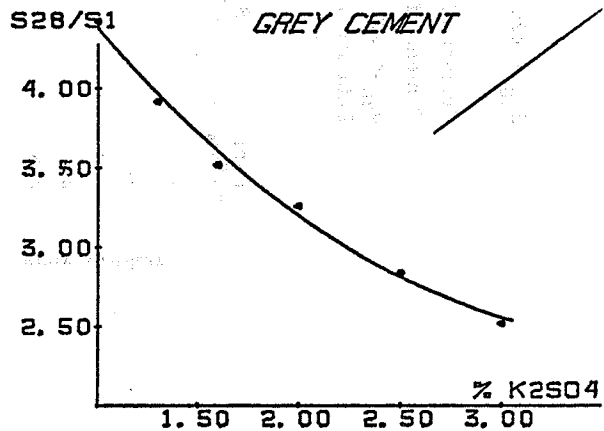
FIG. 9.

$$S_{28} = 420 - 50 \times K_2SO_4 + 2,5 \times C_3S$$

Content of K_2SO_4 in clinker = 1,0 %
Content of C_3S in clinker = 55 %
S_{28} = 507
Data from the Plant = 527 kg/cm^2

	total K_2SO_4 %	S_{28} exp. kg/cm^2	S_{28} calc. kg/cm^2	Δ
grey clinker	1	527	507	20
	1, 3	492	492	0
	1, 6	470	478	- 8
	2	454	458	- 4
	2, 5	420	433	-13
	3	425	408	13
white clinker	0	675	645	30
	0, 3	607	630	-37
	0, 6	583	615	68
	1, 0	557	595	-38
	1, 5	593	570	23
	2, 0	534	545	-11

Mr. P. Jackson

Mr. Vagn Johansen claims that strength drops more than 10% at 28 days when converting from the old wet process to the new dry suspension preheater kilns. It is our experience that these drops are far less dramatic or indeed non existent in practice for the following three reasons:-

1) Burning conditions on the new suspension preheater kilns are normally better and lead to higher C_3 contents in the clinkers.

2) The relationship between % K_2SO_4 and 28 day strength shown can be misleading in that it is unusual to find cements made on old wet process kilns with less than 0.7% K_2SO_4.

3) If a manufacturer has to meet a certain 28 day strength require- ment there are, as Mr. Bryant Mather has suggested, other proced- ures which can be used to achieve this end, and these would in most cases be less expensive than the cost of 150 k.Cal/kg of fuel noted in Mr. Svendsen's paper.

Generally a change to a suspension preheater kiln in practice leads to a product having a similar 28 day strength and improved 3 and 7 day strengths.

Thamesmead