ALKALIS IN CEMENT AND CEMENT MANUFACTURE

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Abstract: The cement manufacturer has been concerned with al-
kalis for many reasons. One of the most challenging
tasks is to produce low alkali clinker from alkali-
containing raw materials.

Increases in operational costs are almost inevitable
and plant operation is often impeded.

With the behaviour of volatile components in modern
kiln systems as a starting point, the possibilities for
reducing the alkali content of clinker and the possible
effects on energy consumption and environment are dis-
cussed.

Key words: Alkalis - clinker production.

1. INTRODUCTION

The cement industry has undergone considerable changes over the
past 10-15 years. Small cement companies have been taken over by
or merged into bigger companies concentrating production on larger
units. Up to the late fifties coal was the general source of en-
ergy, and this was followed by a period with very cheap fuel oil
and gas. This lasted until 1975/77 when industry reconverted to
coal. Today's high fuel prices have necessitated the conversion of
cement plants to the dry and semi-dry processes.

A modern cement plant typically consists of one production unit
with a capacity of 3000 tpd. The trend towards these large pro-
duction units demands extensive preliminary investigations to
prove the technical feasibility and economic viability of a pro-
ject. Cement plants are highly capital-intensive and a feasibility
study involves market research, raw material investigations, se-
lection of plant type, infrastructure and organisation.

Typical data for a modern cement plant is shown in Table I.

TABLE I

Typical data for a modern cement plant

Capacity per year/cement	1,000,000 tons
Type of process: Dry, coal-fired, precalciner kiln	
Fuel consumption/kg clinker	750 kcal
Power/ton cement	95 kWh
Cost of plant	US$ 200 million
Cost per job	US$ 1 million
Cost of product/kg cement	7 cents

The siting of a cement plant is as mentioned governed by many factors, and not always the best raw materials can be selected, especially these days when cement plants have to meet environmental demands.

The main components for manufacturing cement CaO, SiO_2, Al_2O_3, and Fe_2O_3 are often contaminated with the so-called "minor components", the most important of these being MgO, SO_3, K_2O, and Na_2O. Apart from the raw materials the alkalis can be introduced from the fuels, and e.g. sea water.

The alkalis are important for two reasons. The first is the effect on the pyroprocessing of the cement raw mix. The development of kiln systems from wet-process kilns with small dimensions and low production to dry-process kilns with outputs ten times greater and with high fuel economy has drastically affected the behaviour of volatiles. Repeated volatilisation in the burning zone and condensation in the colder parts of the system result in an internal circulation of the volatiles. In order to avoid excess concentrations in this internal circle, special consideration must be given to both raw materials and the process. Marked concentrations may result in build-ups at various points in the kiln system, thereby impeding operation.

The second reason is to be found in the quality of cement produced. If the amount of soluble alkalis in the clinker changes, we know that the strength development of the cement concerned will change. By increasing the alkali content the early strengths will increase while the corresponding 28-day strengths will decrease /1,2,3/. A typical example is given in Fig.1. In many cases cement manufacturers are in markets where only "low alkali" cement can be sold.
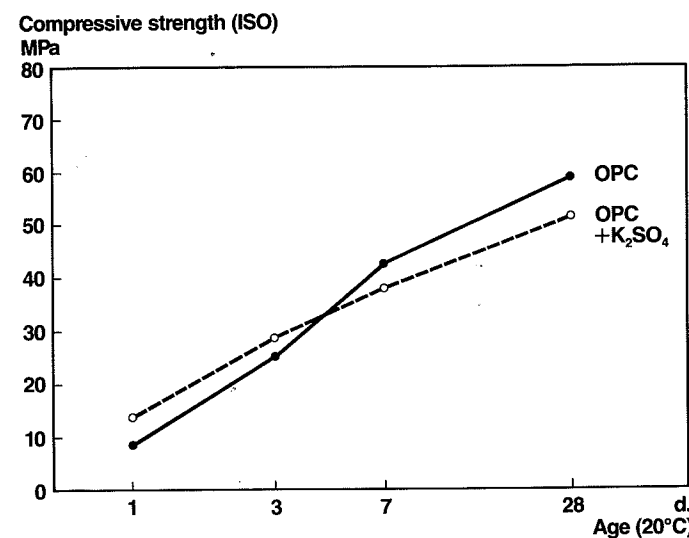

Compressive strength (ISO)
MPa

Fig. 1: Strength development of ordinary portland cement with or without soluble alkalis

Since the deleterious alkali-silica reactions were recognised and described by Stanton in the 1940's, one of the precautions taken in the production of concrete has been to specify "low alkali" cement. Before that time, attempts were sometimes made to remove alkalis from cement clinker for other reasons. A 1929 report /4/ mentions the removal of alkalis to avoid "alkali burns" on concrete workers. The report also lists the difficulties encountered in the operation of a rotary kiln when trying to remove the alkalis.

One of the problems in producing low-alkali cement is the increasing costs. This has also been stressed by Bryant Mather in his paper "New Concern over Alkali Aggregate Reaction" presented at the Reykjavik Symposium in 1975 /5/. In the introduction he states,

"The simple, cheap precaution of specifying 'low-alkali cement', and obtaining it at no increase in price over cement not required to be low-alkali, will no longer be widely available".

In the following we shall deal with the methods available to cement producers for controlling clinker alkali content. Also mentioned are the decisive parameters for volatilisation and removal of alkalis based on experience gained at the newest cement plants.

2. WAYS OF CONTROLLING THE ALKALI CONTENT OF CLINKER

The logical way to produce low-alkali clinker is to use raw materials with a limited content of sodium oxide and potassium oxide. The possibilities are very restricted in some cases, however. The raw materials at site are a determining factor while transportation costs set the limit to the nature and quantity of materials which can be purchased elsewhere by individual producers of cement.

Selective quarrying can be applied in many cases but the resultant reduction in the lifetime of the quarry can affect the economy of the whole operation.

Previously, when kiln dimensions were smaller and gas cleaning less efficient, most of the alkalis escaped into the atmosphere. This was because of the high concentrations of alkalis in the fine part of the dust. Due to the repeated volatilisation and condensation in the internal circulation of the volatiles, most of the alkalis are precipitated in the fine fraction of the dust. Therefore removal of the kiln dust was a way of controlling the amount of alkalis.

In 1942, Woods /6/ reported that average removal of alkalis in 4 dry-process kilns was 61% and 37% for K_2O and Na_2O, respectively, and in 4 wet-process plants it was 51% and 17%. Unfortunately he did not state kiln sizes or the quantities of dust removed. As no problem was created by depositing dust at that time, it is most likely that no dust at all was returned to the kilns in question.

20 years later Goes and Keil /7/ wrote a paper on the conditions for the alkalis during burning. In their paper they compare laboratory experiments with data from 14 different kilns, wet-process kilns as well as dry-process kilns with and without suspension preheater. Regarding the removal of alkalis they concluded that the decisive parameters are the amount of dust removed from the kiln system and the temperature of the exhaust gases. Fig. 2 illustrates the residual K_2O content of the clinker versus the amount of dust removed. (The residual K_2O is expressed as the K_2O percentage of the clinker relative to the K_2O percentage of the kiln feed on ignited basis).
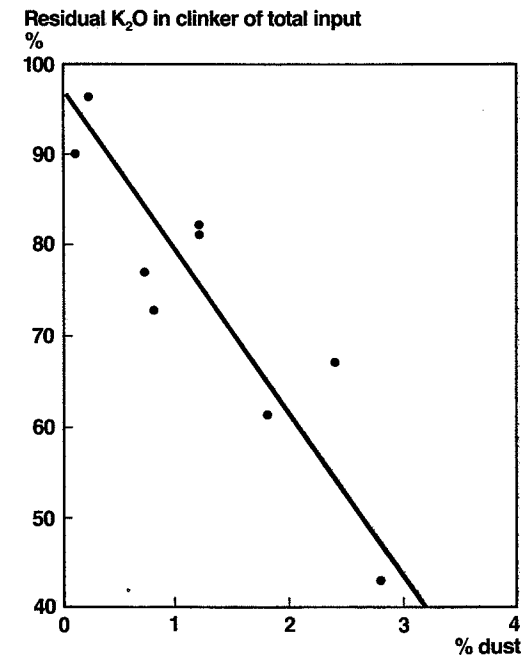
Residual K₂O in clinker of total input %

Fig. 2: Residual K_2O of clinker versus amount of dust removed according to Goes and Keil 1960 /7/.

Modern preheater kilns are completely closed with regard to volatile matter in the raw materials. And the increased concentration of the alkalis in the fine fraction of the dust to the extent found in the older and smaller kiln systems does not apply any more. Therefore the removal of kiln dust is no longer an effective control parameter.

Fig.3 shows the internal circulation of the alkalis which enter the system with the raw materials. In the raw mill the concentration increases due to the uptake of kiln gases which are used for drying the raw materials. Together with the dust from the precipitator the raw mix is fed to the preheater. In the preheater most of the volatiles from the burning zone of the kiln will condense and re-enter the kiln.
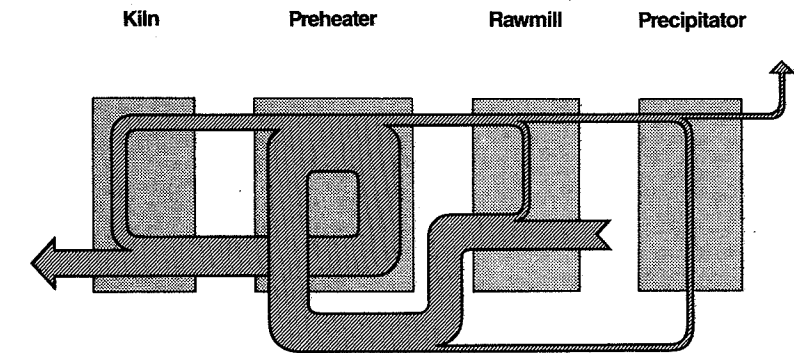
Fig. 3: Sketch of the internal cycle of the volatiles

A statistical study of a large number of dry-process kilns including suspension preheater kilns and precalciner kilns, all without bypass, shows that the evaporation of K_2O in the kiln burning zone can be regarded as the result of three contributing factors /8/:

A   From the amount of K_2O combined as KCl. As the Cl content in the internal cycle is normally high, this contribution is considerable. KCl evaporates completely at the temperature of the burning zone.

B   From the K_2O which has volatilised and condensed – therefore taking part in the internal cycle – but not as chloride. Of this, 80-90% evaporates in the burning zone.

C   Finally the contribution from the $K_2O^{x)}$ contained in the fresh raw mix. Depending on the chemical composition of the raw mix and the temperature distribution in the burning zone, this will evaporate with 20-50% of the input.

The Na_2O evaporates with only up to 20% of the input. All this falls in line with our general experience – potassium oxide evaporates more easily than sodium oxide, and chloride has a positive effect on the volatilisation of alkalis.

When bypassing all or part of the kiln gases the volatiles are not condensed on the new feed in the preheater and the internal cycle is interrupted. In bypasses exceeding a certain limit it is to be expected that only the contribution from Point C mentioned above is effective. An upper limit for the reduction of the input of K_2O and Na_2O is consequently to be expected. These limits are in the order of 50% and 20% for K_2O and Na_2O, respectively.

x)   In this context K and Na are represented by their oxides.

3. PARAMETERS DECISIVE FOR ALKALI EVAPORATION

Decisive parameters for alkali evaporation in the burning zone are temperature distribution, retention time, and chemical composition of the kiln feed.

Laboratory experiments have shown, and practical experience confirmed, that burning a given cement raw mix to the same content of free CaO in the clinker results in the same residual alkali content regardless of temperature treatment. In other words, burning at high temperature for a short time or burning at a lower temperature for a correspondingly longer time gives the same degree of alkali removal.

The temperature effect is shown in Fig.4. The K_2O content of the clinker is plotted versus the calculated burning temperature. The data is from a precalciner kiln during a period with constant K_2O content of the kiln feed.
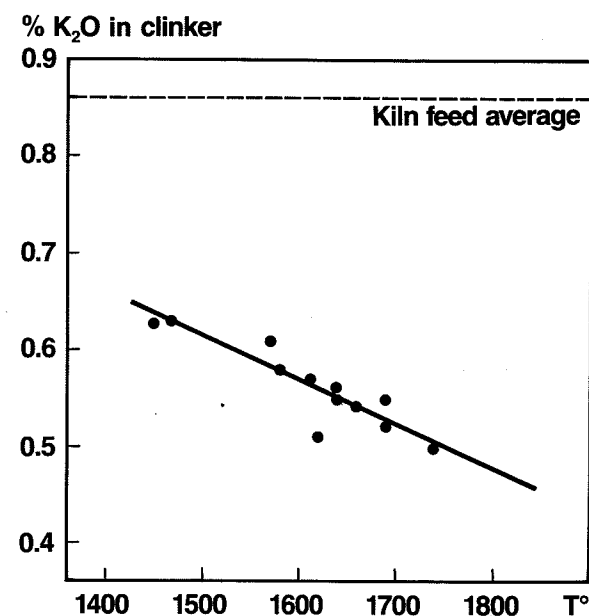

Fig. 4: % K_2O of clinker versus estimated average burning zone temperature data from a precalciner kiln

Experiments confirmed in practice have demonstrated that a high concentration of CaO in the kiln feed, e.g. represented by a higher content of C_3S, increases the volatility of the alkalis.

Also the physical conditions of the burning zone may have an effect on the total amount of alkalis which can be evaporised from the charge.

Comparing a small kiln with a large kiln and assuming a constant rate of evaporation per surface unit, it can be shown that the total amount of alkalis removed is inversely proportional to the radius of the kiln and to the kiln charge. This is illustrated in Fig. 5. Increasing the kiln dimensions and keeping the kiln charge constant allows for elimination of a smaller amount of the total alkalis in the large kiln. In the precalciner kilns the kiln charges are increased approx. 50% relative to the standard applied in other kiln types, which will further impede the alkali evaporation.

This might be part of the explanation why the alkali removal seems to be more effective in the small kilns in production 20 or more years ago.
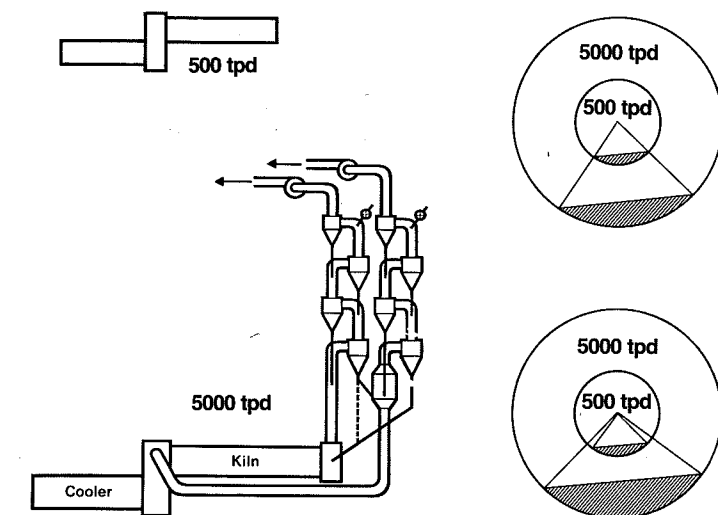

Fig. 5: Comparing kilns of different sizes. The ratio between surface area and volume of the kiln charge decreases with increasing kiln dimensions. Increasing the kiln charge has a similar effect.

4. EXPERIENCE WITH ALKALI BYPASSES

It is only in recent years that kiln systems have been fitted with large bypasses to remove alkalis from the clinker produced. Earlier, bypasses were only rarely used, mainly for removing sulphur or chlorine, and designed for bypassing 10-15% of the kiln gases. There is an upper limit to the size of bypasses for suspension preheater kilns, but with precalciner kilns it is possible to bypass 100% of the kiln gases. Optimism with regard to the efficiency of these large bypasses for removing alkalis has proved only

partly justified. This optimism was based on the fact that the high concentrations observed in the internal cycle in conventional suspension preheater kilns gave rise to the belief that by merely bypassing some of the kiln gases a considerable part of the alkalis would thus be removed. The fact that most of the cycling volatiles are condensates and that their concentration is considerably lower when operating with an open bypass had been overlooked. The results obtained in practice are shown in Table II, the data being from three ILC (In-Line Calciner) kiln systems. The kiln layout is shown in Fig.6.
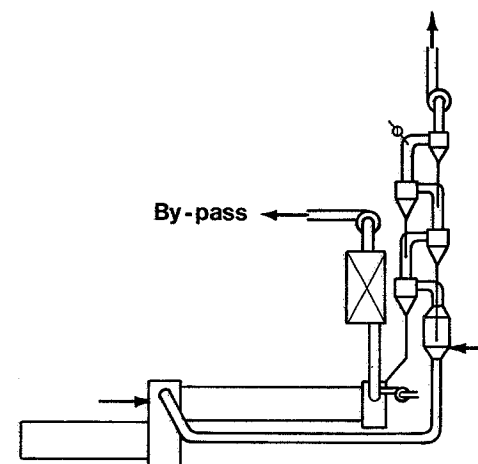

Fig. 6: In-Line Calciner kiln

TABLE II
In-Line Calciner (ILC) kilns

	Plant A	Plant B	Plant C
Production tonnes/24 hours	2360	1590	2050
% bypass	40	40-50	40-60
x) R_{K_2O}, residual K_2O in clinker (%)	70	70	70
	By increasing the dust losses from the bypass R_{K_2O} decreased to 60%	By addition of $CaCl_2$, R_{K_2O} between 35% and 50% was obtained.	Hard burning and $C_3S > 60\%$ resulted in $R_{K_2O} \sim 55\%$.

x) $R_{K_2O} = \dfrac{\% \ K_2O \ (clinker)}{\% \ K_2O \ (kiln \ feed, \ ignited)} \ 100\%$

The table shows average monthly figures for the residual K_2O of the clinker expressed as a percentage of input. In all cases, 70% of the added K_2O is found in the clinker. Experience with all kilns seems to indicate that no increase in the removal of K_2O is obtained by raising the capacity of the bypass beyond approx. 60%. The only measurable effect is an increase in fuel consumption. By analysing the daily averages in relation to operational conditions it was found that by increasing the dust losses via the bypass, the removal was more effective. This applied to Plant A for a short period during which the amount of dust was three times normal level. The addition of $CaCl_2$ also improves alkali reduction, and finally, an increased CaO content of the clinker together with hard-burning improves the removal of alkalis.

Experience in practice also demonstrated that the reduction of Na_2O in the clinker is negligible - only 0-20% of input removed.

An analysis of the data, not yet completed, indicates that the general assumption that the evaporation factors are constant for a given set of raw materials and a given kiln is not valid. It appears to be a function of bypass size. The evaporation factors in relation to suspension preheater kilns without precalciner can only be applied to precalciner kiln systems within certain limits.

The fact that the large alkali bypass is somewhat less effective than anticipated seems to confirm this. Practical experience has shown that the most effective means of reducing the alkali content of the clinker apart from $CaCl_2$ - addition is hard burning of the raw mix corresponding to clinker with a high C_3O content.

This, however, also entails a number of problems, the greatest being the effect on the environment. Goverment restrictions on the emission of NO_x, etc. are becoming increasingly stringent. Increased production of NO_x is an inevitable consequence of hard burning. Fig. 7 gives an example from a precalciner kiln with bypass. It shows the daily mean values of residual K_2O in the clinker in per cent of K_2O entering the kiln compared with the concentration of NO_x in the exhaust gases. Depending on local emission standards this may be extremely important to the individual cement producer.

The production of low-alkali clinker entails other operational problems such as lining durability: the higher the burning temperature, the greater the consumption of lining materials.

Hard burning as well as the abovementioned chemical composition may also result in a clinker granulometry (dust clinker) which does not ensure optimum operational conditions in the clinker cooler and also requires more energy for grinding the clinker to cement. Hard burning will also lead to a greater heat loss from the exhaust gases in the bypass, thus resulting in higher fuel consumption. The additional costs due to the bypass are (depending on the amount of dust) around 2 kcal/kg clinker for each per cent of kiln gases bypassed. 50% bypass will thus mean an additional consumption of 100 kcal/kg clinker or an increase in fuel consumption by more than 12%.
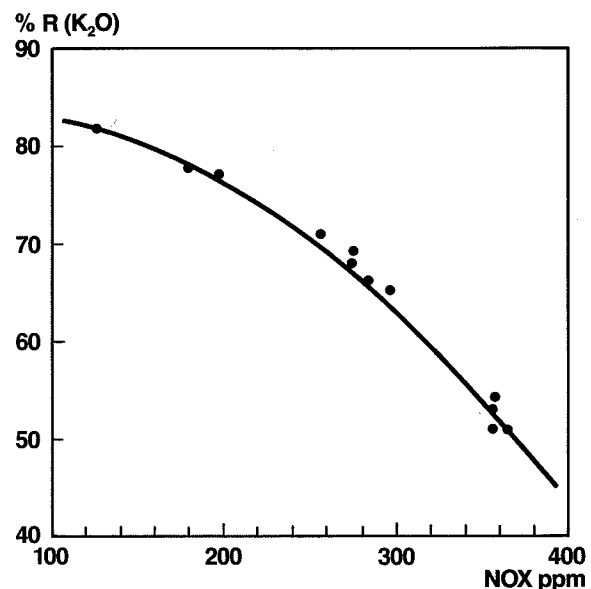
Fig. 7: Residual K$_2$O in clinker versus NO$_x$ content of gases
in the stack.

In cases where the high content of Na$_2$O and K$_2$O in the raw
materials makes it impossible to produce low-alkali clinker even
with a larger bypass, it will be necessary to add CaCl$_2$ or some
other source of Cl.

All this results in a quite considerable increase in the cost of
cement manufacture. For example, the amount of CaCl$_2$ required to
remove 0.15% K$_2$O from the clinker would cost between $1 and 2
(1982) per tonne clinker. This should be viewed against the fact
that the normal output these days is 3000 t/d.

The expected increase in the cost of making low-alkali cement was,
as mentioned in the introduction, expressed very clearly by Bryant
Mather at the Reykjavik conference in 1975. On that occasion he
pointed out that the renewed interest in alkali-silica reactions
was due among other things to the fact that one can no longer ex-
pect to obtain low-alkali cement at the same prices as for cement
whose alkali content need not be low. This corresponds to the
statement made by D.E. Damp /9/ at the 5th International Confer-
ence on Alkali-Silica Reactions in 1981: "The cement producer can
only make low-alkali cement through a more costly process".

5. ALTERNATIVES TO THE REMOVAL OF ALKALIS FROM THE CLINKER

In his opening speech at the 5th Conference on Alkali-Silica Re-
actions, D.E. Davis /10/ mentioned that it may be possible to find
expansions in concrete even when low-alkali cement as well as "inert
additives" are used. This means that a durable concrete is not en-
sured merely by specifying low-alkali cement. The increased cost of
making low-alkali clinker may then have been in vain.

In cases where the materials are in fact reactive the problems may
be solved differently, e.g. by applying additives. It is interesting
to learn that it was already discovered by Stanton /11/ that the ad-
dition of finely ground reactive aggregates may help to prevent da-
mage to the concrete due to alkali-silica reactions.

It is of course interesting that the same material may have undesir-
able effects as well as the opposite depending on the particle size
distribution, and it is natural to compare this fact with the many
results showing that the addition of materials similar to puzzolana
has a favourable effect on the durability of the concrete when there
is a risk of alkali-silica reactions.

At a time when dumping of waste materials such as fly ash is causing
problems to the community, an obvious solution is to use mineral ad-
ditives to prevent damage to concrete caused by alkali-silica reac-
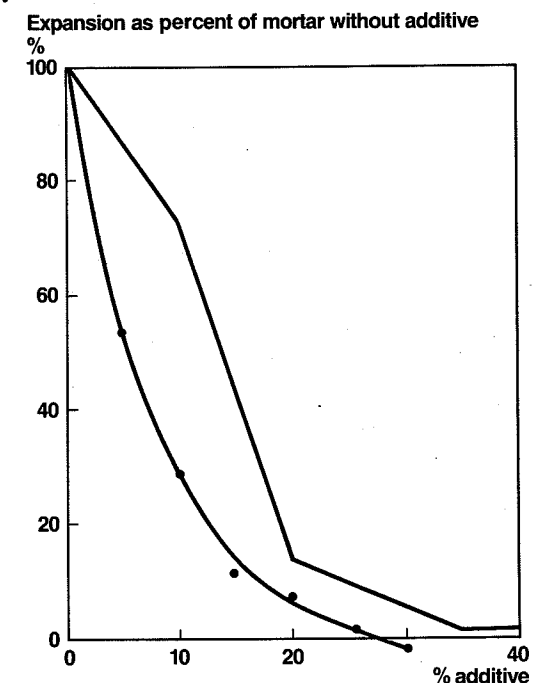tions (Fig. 8).

Fig. 8: Expansion of the mortar relative to mortar without addition.
Full curve with addition of fly ash /12/. Curve with dots,
addition of silica flour /13/.

Not only the individual cement producer, but also the community as a whole stand to gain from such solutions.

6. CONCLUSION

The reduction of alkali in clinker produced from large kilns with large bypasses has not been as pronounced as expected. This is because such kiln systems were based on experience gained from preheater kiln systems without bypass. Analyses of statistical data from a great number of kilns have shown that the high evaporation coefficients are due partly to a large amount of circulating alkali chlorides. In kiln systems with bypass which exceed a certain size the internal circulation is stopped and only the proportion of the alkalis which evaporates 'first time' can contribute to the alkali reduction. Investigations have shown that, contrary to previous assumptions, the evaporation coefficient is not constant and independent of the size of the bypass.

The results attained in practical operation show that Na_2O can be reduced by up to 20% of the Na_2O admitted and that up to some 30% of the K_2O admitted can be removed. Practical experience also seems to show that alkali bypasses become far less efficient once their size exceeds 60%, the alkali reduction in such precalciner kilns being only slightly higher while fuel consumption is increased.

The conditions which ensure the most effective reduction of the alkali content in clinker also make kiln operation more costly. It is therefore unrealistic to expect that low-alkali cement will continue to be available at the same price as cement with no limitation of alkali content.

From the relevant literature it is known that damage to concrete due to alkali-silica reactions can be counteracted by applying mineral aggregates.

Soon after the connection between alkali content and reactive aggregates had been discovered, it become known that the addition of finely ground reactive aggregates had this effect. From various publications there are many examples of fly ash, slag and puzzolana having similar effects. Following the oil price jump and the consequent increase in coal consumption, the rapidly increasing amount of fly ash produced is becoming a problem. One means of disposing of fly ash is by using it as an additive in cement.

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