ALKALI - AGGREGATE REACTION

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1981

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ALKALI REDUCTION IN CEMENT KILNS

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SYNOPSIS

Certain volatile components, mainly potassium, sodium, sulphur and chloride evaporate and condense with temperature changes in the kiln until an equilibrium is reached. A simple mathematical model has been developed to predict the behaviour of volatile matter in new or altered kilns.

Various designs for kilns are discussed with regard to the reduction of alkalis in the clinker which is of importance not only to reduce the risk of the alkali-aggregate reaction but also to improve the strength development which is adversely affected.

Low alkali cement can now be produced by a dry process system economically and without loss of production.

SAMEVATTING

Sekere vlugtige komponente, hoofsaaklik kalium, natrium, swael en chloried verdamp en kondenseer, as gevolg van temperatuurwisseling, in die oond totdat ewewig verkry is. 'n Eenvoudige wiskundige model is ontwikkel om die gedrag van vlugtige materiaal in nuwe of gemodifiseerde oonde te voorspel.

Verskillende ontwerpe vir oonde word bespreek met betrekking tot die vermindering van alkalië in klinker, iets wat belangrik is nie slegs om die risiko van 'n alkali-aggregaatreaksie te verminder nie maar ook om die ontwikkeling van sterkte, wat nadelig geraak is, te bevorder.

Lae alkalisement kan nou met 'n droëprosesstelsel ekonomies en sonder verlies van produksie vervaardig word.

By-Poss

FIGURE 4

The preheater valves are generally small and, of course, very small for 4 stages of cyclones as the valves for each stage theoretically must be multiplied by each other to give the total valve. Practice does not fully follow this formula, partly due to the circulation of dust from one stage to another.

Precipitators have rather big valves, which may seem surprising. The valves are based on material balances and not on direct measurements on the gas after the precipitator. The low apparent efficiency of precipitators in respect of volatile matter could be due to such matter being present as vapours or ultrafine particles.

When the object is to obtain a low concentration in the clinker of a certain volatile constituent, i.e. a low value of R, high evaporation factor, and a big valve, V, are required as seen in Figure 2.

To obtain sufficient evaporation in practice, it is often necessary to increase the burning temperature, which may be done by increasing the silica ratio.

Other means of obtaining high evaporation factors are to decrease the belite content of the clinker, by increasing the lime saturation factor, and to reduce the sulphur content of the fuel to create a low sulphur/alkali ratio.

Furthermore, the evaporation can theoretically be increased by adding $CaCl_2$ to the raw mix, but this can in preheater kilns cause clogging and coating problems.

In the following the various kiln systems and their capabilities for reducing the alkali content of the clinker are discussed.

2. LONG KILNS

For many years, the classical wet kiln for small and medium outputs of up to 800 tons per day was the dominant type of cement kiln. It is equipped with a system of internal heat-exchange fittings comprising slurry preheater, garland chains and a cross system. Typically this kiln operates at an exhaust gas temperature of about 170°C, and a specific fuel consumption of 1300–1400 kcal/kg. It is essential for its proper functioning that the slurry be plastic.
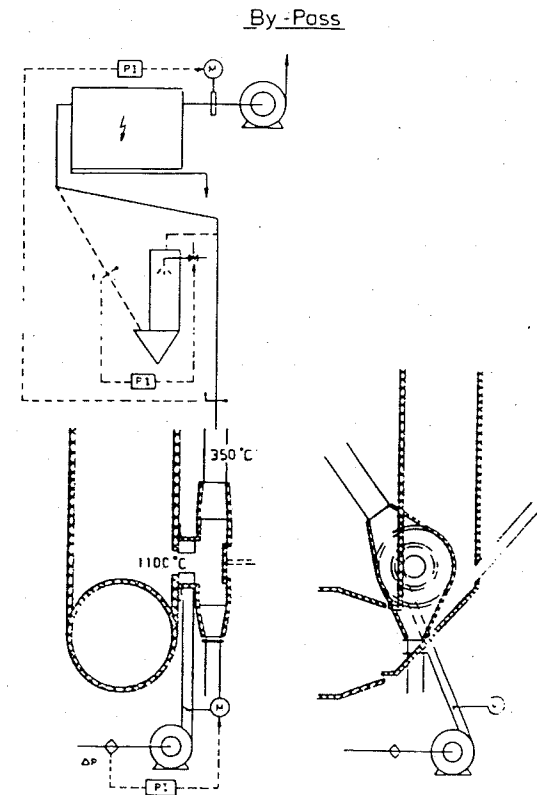
Because of the low dust burden of the gases, the alkalis condense and solidify at the cold end of the kiln as separate and minute salt particles which to a large extent penetrate the internals and reach the precipitator. The electrostatic precipitator possesses the characteristic property of precipitating the dust selectively according to particle size, and hence, the fine and salt-rich fraction of the dust concentrates at the rear end of the filter.

TABLE 3 : Relationship between alite and belite content and alkali volatility

Volatility of K and Na		alite clinker	belite clinker
K	unsulphated	high	medium/high
	sulphated	low	low
Na	unsulphated	medium/high	medium/low
	sulphated	medium/low	low

TABLE 1: Melting Points & Boiling Points, °C

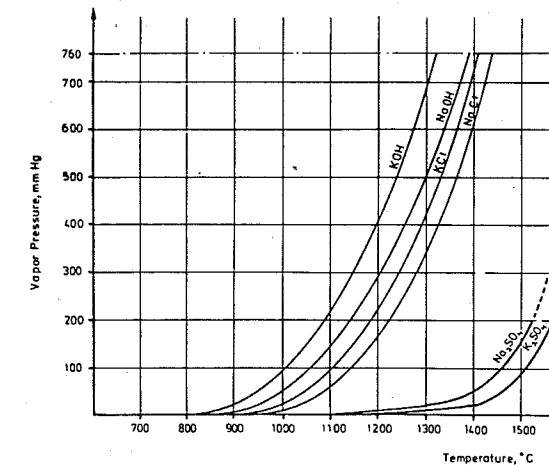| COMPOUND	K		Na	
	Melting Point	Boiling Point	Melting Point	Boiling Point
Oxide	decomp.	350	sublim.	1275
Carbonate	894	decomp.	850	decomp.
Sulphate	1074	1689	884	–
Chloride	768	1411	801	1440
Hydroxide	360	1320	328	1390

FIGURE 3

tion, fineness, coarse silica, fluxes and so on) of the raw mix, and thus in the burning temperature, influences the evaporation. Furthermore, the composition of the salts in which the volatile matter is present is very important. For instance, it is well-known that in most kilns, the volatility of chlorides is nearly 100 per cent and that chloride facilitates the evaporation of alkalis. It is also known that sulphur reduces the evaporation of alkalis as is to be expected owing to the relatively lower vapour pressure of the sulphates.

Average values for factors such as evaporation are shown in Table 2. In practice it is found that the undermentioned characteristics can vary considerably according to the working conditions in the kiln such as the flame form, or the excess air.

Recent laboratory experiments[2] have shown that the volatility of the alkali compounds also depends to a certain extent on the alite and belite content in the clinker. Table 3 shows the results of these experiments:

The values for the various valves given in Figure 4 are based on a number of complete mass balances. Considering the fact that a valve of 1.0 means that nothing is collected, it will be noticed that the valve for the kiln proper can vary widely according to the type of kiln.

The size of the valve depends mainly upon whether the component is condensed as droplets or on solid particles, and on the size of such particles. A high dust load in the gases causes the volatile matter to condense on the surface of the dust particles instead of forming small separate particles, and this will greatly affect the size of a valve.

TABLE 2 : Typical Average Values for ε and V

	Symbol	K_2O	Na_2O
Evaporation Factor	ε	0.60	0.40
Kiln Valve , wet nodule-op. kiln	V_o	0.50	0.70
— , wet dust-oper. kiln	V_o	0.40	0.60
— , long dry kiln	V_o	0.20	0.50
— , 1 stage kiln	V_o	0.55	0.80
— , 2 stage kiln	V_o	0.70	0.85
— , 4 stage kiln	V_o	~ 1	~ 1
— , pre-calciner kiln	V_o	~ 1	~ 1
Cyclone Preheater Valve , 1 stage	V_c	0.35	0.50
— — — , 2 stages	V_c	0.20	0.45
— — — , 4 stages	V_c	0.10	0.40
Dedusting Cyclone Valve	V_c	0.60	0.70
Raw Mill Valve	V_m	0.60	0.80
Cooling Tower Valve	V_{kt}	~ 1	~ 1
Elec. Precipitator Valve	V_f	0.40	0.70

in the by-pass contains valuable energy which must be compensated for by extra fuel input to the kiln. Furthermore, the dust waste represents a loss of partially calcined raw material. For a 4-stage-SP kiln it can be assumed that each 1 per cent of by-pass costs about 5 kcal extra energy input per kg of clinker and an additional loss of about 2 g of dust per kg of clinker.

The dust collected in the by-pass filter can, of course, not be re-introduced into the process, since it contains most of the salts which must be eliminated from the system. Often the dust is so rich in chlorides that its use as a fertilizer is precluded. There is usually no other alternative but to granulate and dump the dust in a remote part of the quarry.
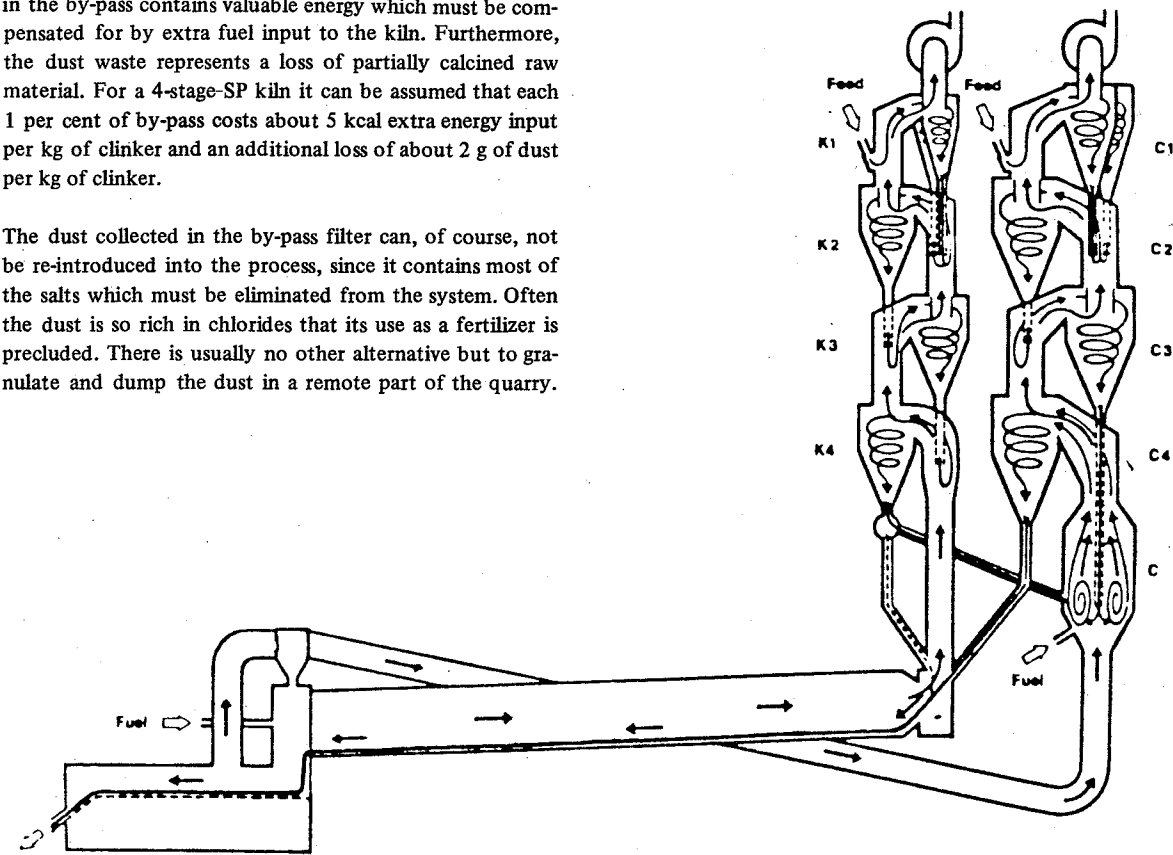

FIGURE 5: F L S Standard Kiln. Flow diagram

FIGURE 6

4. PRECALCINER KILNS

The characteristic feature of the precalciner kiln is that the precalcination is carried out by application of secondary firing in a stationary unit. Most precalciner systems allow up to 95 per cent precalcination on the raw meal.

The behaviour of the volatiles in the precalciner system is found to be much the same as in a conventional 4-stage SP-kiln.

The temperature in the calciner is so low (850–900°C) that the alkalis are not evaporated here to any noticeable degree.

The evaporation is confined to the burning zone, and there are indications that the evaporation factors tend to be on the low side in precalciner kilns – probably owing to the relatively low thermal load and short residence time of the clinker in the burning zone.

An interesting feature of the precalciner kilns is the efficiency of by-pass with respect to reducing the volatile compounds in the clinker. Since all evaporated material is contained in a far smaller volume of kiln gas compared to conventional SP-kilns (0.45 against 1.20 normal m^3/kg clinker), less hot gas has to be wasted to achieve a certain degree of alkali reduction. Hence, the energy penalty is
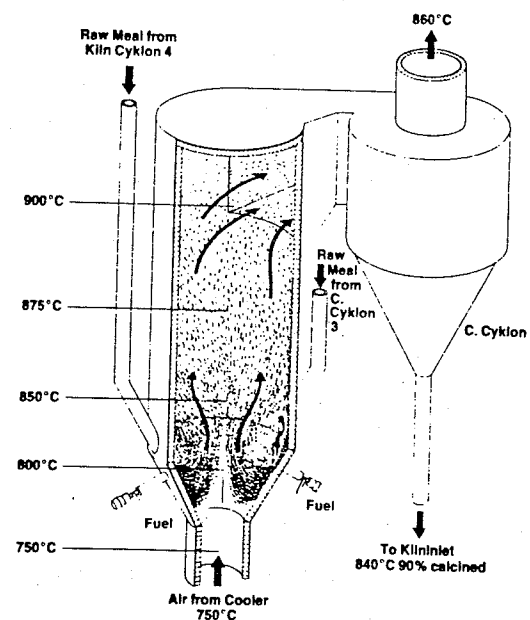
For wet kilns of higher output the principle of producing dust-free nodules in the chains and gently processing these nodules throughout the kiln can no longer be maintained. The kiln is in this case equipped with a dense chain system and the feed is dried out completely and even preheated to several hundred degrees Celsius in the chains. As a result, and owing to the high gas velocity, the dust burden at the upper end of the kiln is high and the condensation of salt vapour will mainly occur on the surface of the dust particles. Thus the selectivity of the electrostatic precipitator is reduced and alkali reduction is more costly and troublesome because of the larger quantity of dust to be wasted. This is illustrated in Table 4.

In the long, dry kiln conditions comparable to those of the large dust-operated wet kiln prevail. Yet, the dust burden is even higher, and the basis for alkali reduction even less favourable.

3. PREHEATER KILNS

If the dry kiln is equipped with a cyclone preheater (SP), the cost of the kiln installation becomes lower and the heat economy is improved in comparison with the long kilns. A drawback is that the preheater is very efficient at trapping the alkalis and recycling them to the kiln. As a result, heavy internal circulation is often encountered in the preheater kilns and the alkalis almost quantitatively end up in the clinker, unless special precautions are taken. The filter dust from preheater kilns is only slightly enriched with respect to alkalis and only very limited alkali reduction may be achieved by discarding this dust.

Since the natural valves may not be sufficient for a preheater kiln, an artificial valve can be made by removing part of the kiln gases in a by-pass before the preheaters as shown in Figure 4, page 3.

The gases to be by-passed are diverted from the main gas flow at a point of the riser pipe just above the kiln inlet. To avoid encrustation in the ducts, the gases are immediately quenched by mixing with 3 times as much cold air. The by-pass gases are subsequently dedusted in an electrostatic precipitator, normally after conditioning in a cooling tower.

By-passes are extensively used for controlling the alkali content of the clinker in modern kiln systems. For a conventional 4-stage SP-kiln, a by-pass should not exceed 35 per cent of the kiln gas. Otherwise insufficient gas will be available for the preheating of raw meal in the cyclones. With normal alkali volatility, a by-pass of this size gives a reduction in the clinker alkali to about 2/3 the theoretical maximum value derived from the concentration in the kiln feed.

Unfortunately, the operation of a by-pass imposes certain penalties on the cement producer. The hot kiln gas wasted

TABLE 4 : Alkali reduction by dust waste in wet kilns

		%Dust/feed	Dust returned	Dust wasted	Clinker
	Nodule-operated kiln Clinker output: 700 t/d Heat consump: 1350 kcal/kg Back-end temp: 190°C	Return: 4 Waste: 0	K_2O 15.30 Na_2O 1.65 SO_3 16.63		K_2O 0.90 Na_2O 0.35 SO_3 0.72
Kiln feed: K_2O 0.67 Na_2O 0.25 SO_3 0.12		Return: 0 Waste: 1.8		K_2O 12.07 Na_2O 2.24 SO_3 9.48	K_2O 0.72 Na_2O 0.32 SO_3 0.46
Coal: K_2O 0.24 Na_2O 0.15 SO_3 2.75	**Dust-operated kiln** Clinker output: 1700 t/d Heat consump.: 1450 kcal/kg Back-end temp.: 240°C	Return: 10 Waste: 0	K_2O 3.43 Na_2O 0.52 SO_3 2.89		K_2O 0.95 Na_2O 0.35 SO_3 0.75
		Return: 4 Waste: 5	K_2O 1.56 Na_2O 0.38 SO_3 1.68	K_2O 2.86 Na_2O 0.52 SO_3 3.68	K_2O 0.78 Na_2O 0.34 SO_3 0.48

independent of the size of the by-pass. At a kiln diameter of 6 metres, the output will be about 9000 metric tons per day.

The advantages mentioned above are also obtainable in cases where the raw materials are economically processed according to the wet method. In such cases the slurry is treated in a slurry filtration plant and drier crusher.

5. THE EFFECT OF ALKALIS ON THE QUALITY OF CEMENT

High alkali content is undesirable not only because of the alkali-aggregate reaction but also because of the influence of alkalis on the strength development of cement.
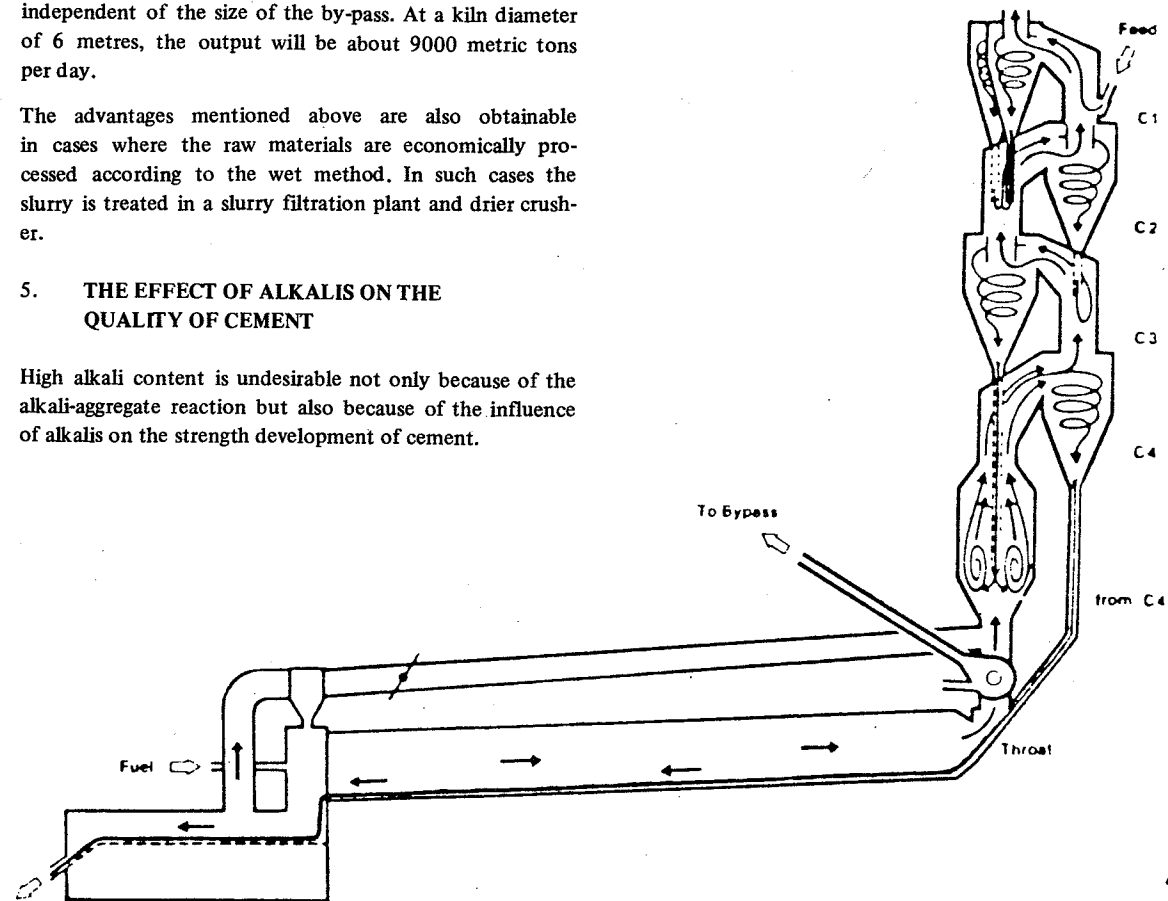

FIGURE 10 : Kiln with variable bypass to control from 0−100% of kiln gases
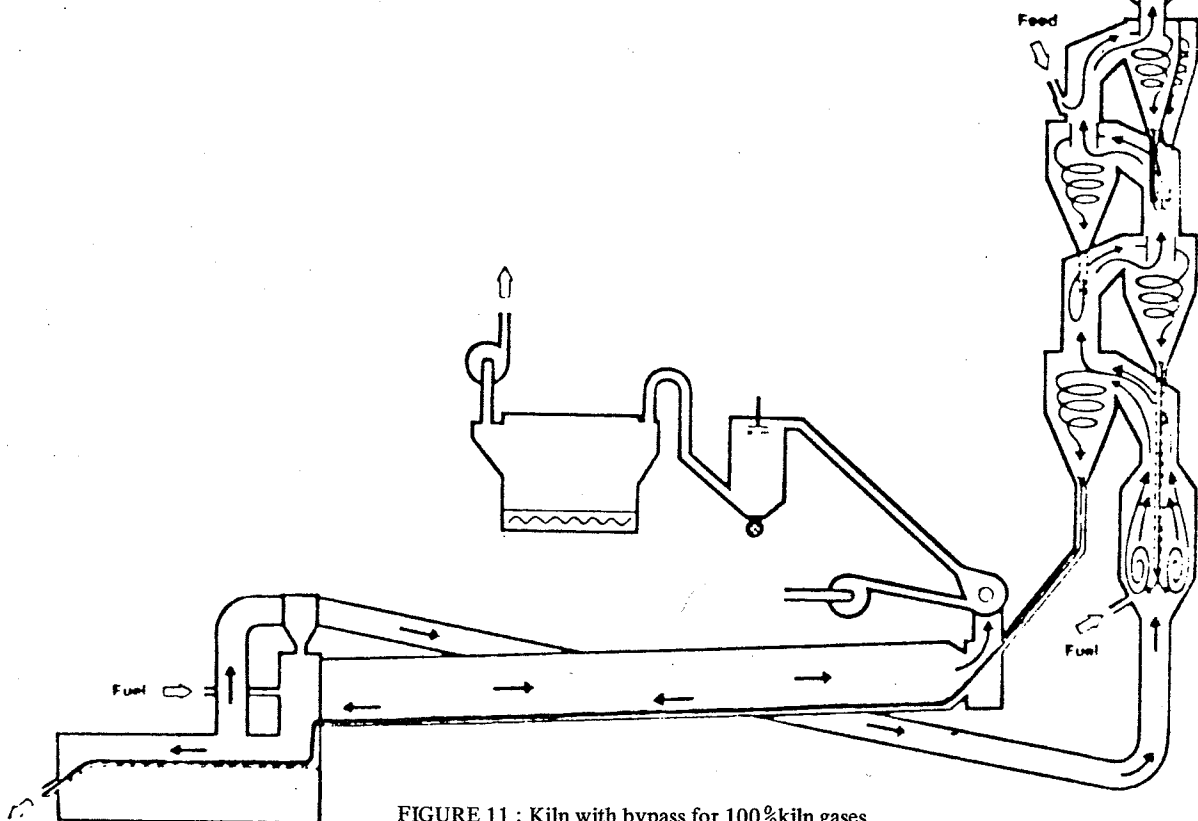
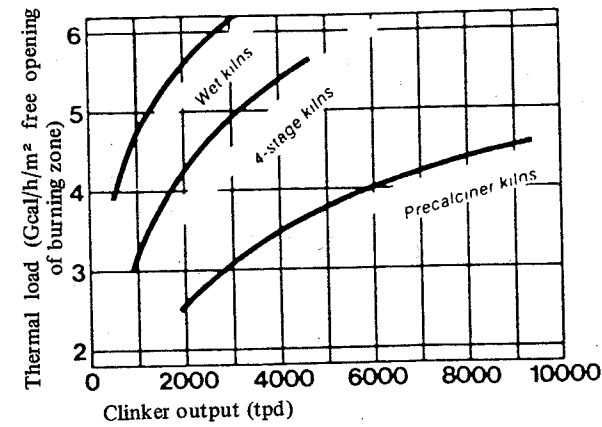

FIGURE 11 : Kiln with bypass for 100% kiln gases

FIGURE 7

also less and amounts to only about 1.7 kcal/kg clinker per 1 per cent of by-passed gas.

Figure 8 shows the alkali reduction as a function of the amount of by-passed gas, expressed as a percentage of the total gases from the system. The graphs assume 60 per cent volatility for K_2O and 40 per cent volatility for Na_2O.

Where a minor alkali reduction in the clinker is necessary, a bypass of up to 30 per cent on a standard precalciner kiln will normally remove 30−35 per cent of the alkali content in raw materials, enough to ensure low-alkali clinker production at many plants.

The precalciner system shown in Fig. 10 is the most convenient if a large and variable by-pass is required for alternating production of low alkali and ordinary Portland cement clinker. The by-pass can be varied from 0 to 100 per cent without disturbing the system.

Maximum alkali reduction is achieved in a kiln where all gases are by-passed (Fig. 11). The additional energy cost is less than about 150 kcal/kg clinker. In a precalciner installation with separate calciner and 100 per cent by-pass, production of low alkali clinker is consequently possible with raw materials with an alkali content about 50 per cent higher than for an ordinary 4-stage SP-kiln.

The by-pass loss also depends upon the dust loss through the by-pass, which is usually lower than in the 4-stage kilns and in precalciner kilns passing all combustion air through the kiln. Compared to the 4-stage kiln the amount of smoke gas is 60−70 per cent lower and the kiln cross section area only 30−40 per cent smaller, with the result that the smoke gas velocity and also the dust loss in the system shown in Figs. 9, 10 and 11 are minimized.

It may be added that by-passing the kiln gas does not reduce the specific output of the kiln tube, which at 90 per cent precalcination is 3,6 − 4 metric tons per day/m^3
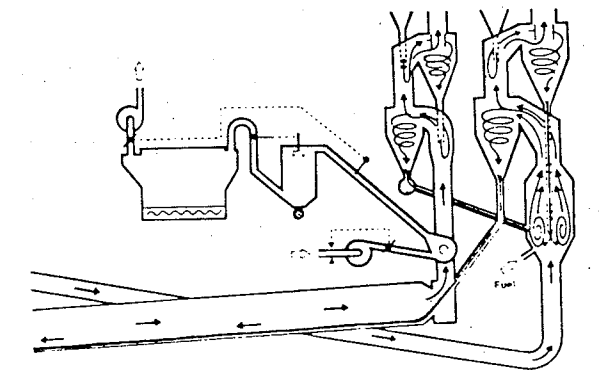

FIGURE 9 : Standard kiln-bypass for 0−30% of kiln gases
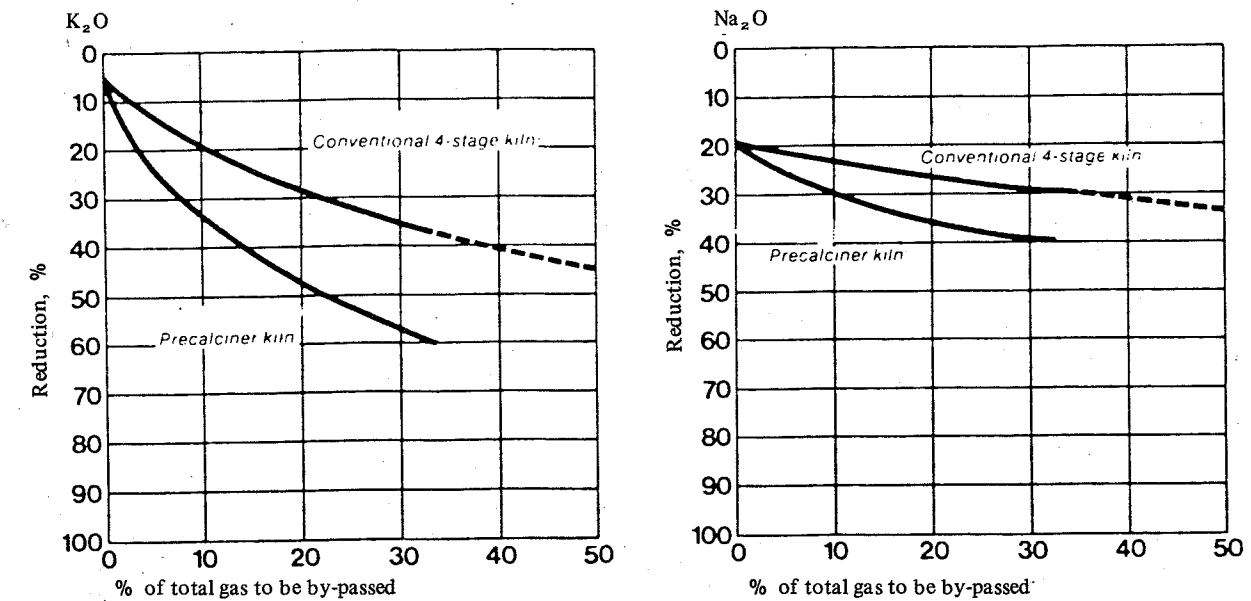

FIGURE 8

6. SUMMARY

The manufacture of low-alkali cement was previously confined to wet or semi-wet process systems and raw materials possessing good nodule strengths.

Today, however, low-alkali cement can be economically produced in dry process systems using a kiln with separate precalciner and full or variable by-pass of kiln gases. The specific fuel consumption of this system does not exceed about 900 to 950 kcal/kg clinker.

The system provides a theoretical minimum content of alkali in clinker determined by the volatility of the alkalis at sintering temperature. The by-pass does not reduce the specific kiln production.

The system provides improved 28-day strengths of the cement. The strength improvement can be predicted [3] based on a formula developed by regression analysis of strength-analysis data.

The precalciner system can be used even when the raw materials are prepared by the wet method. The slurry is in this case filter-dried and powdered prior to burning.

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3. OSBAECK B *Der Einfluss von Alkalien auf die Festigkeitseigenschaften von Portland Cement*, Zement-Kalk-Gips 32, 1979 p 72–77.

4. POLLITT H W W and BROWN A W *The distribution of alkalis in Portland Cement Clinker.* Proc. of 5th Int. Symposium on the Chemistry of Cement, Tokyo, 1968.

5. SVENDSEN J *Alkaliarmer Zement aus Hochalkalirohstoffen mit Energiewirtschaflich günstiger Verfahrenstechnik*, Zement-Kalk-Gips 31, 1978.

The alkalis in clinker are found partly as soluble sulphates and partly built into the clinker minerals. According to present knowledge, the portion found as readily soluble sulphates is influencing the strength development much more strongly than the built-in part. There are, however, a few examples of clinker of extremely high built-in alkali content which behave differently to what could be expected from their composition. A satisfactory explanation of this fact is still to be found, but a possibility is that an excessive concentration of alkali in the C_3A phase reduces its hydraulicity so much that it markedly effects the strength development.

In the FLS laboratory regression analyses on strength and composition data have been made for 31 cements prepared from 31 plant-produced clinkers of different origin and composition. A very surprising result was that 75 per cent of the variation in the 28-day strength measured by the Rilem-Cembureau method could be ascribed to variations in the content of *soluble alkalis*.

The C_3S content proved, surprisingly, only to be the second most important strength parameter. Figure 12 shows the ability of the regression model to fit the strength data.

The model shows that the negative effect of soluble alkalis on 28-day strengths is about 100 kp/cm² per 1 per cent increase in the content of soluble alkalis, expressed as K_2O equivalents ($\overline{\overline{K}}_S$). The regression analyses also indicated positive effects of alkalis on the early strengths, so that the general effect of alkalis on strength development can be illustrated as in Figure 13. The effect on the early strength is in the order of magnitude of 40 to 60 kp/cm² per 1 percent increase in $\overline{\overline{K}}_s$.

The calculation of water-soluble alkalis ($\overline{\overline{K}}_S$) is empirical and derived from data published [4] by Pollitt & Brown in the Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo 1968.

Model: $\sigma_{28}^* = 520 - 100 \cdot \overline{\overline{K}}_s + 1{,}5 \cdot C_3S$

Actual strength kp/cm²

400 450 500 550 600 650 kp/cm²
* ISO-RILEM (kp/cm²)   Estimated strength
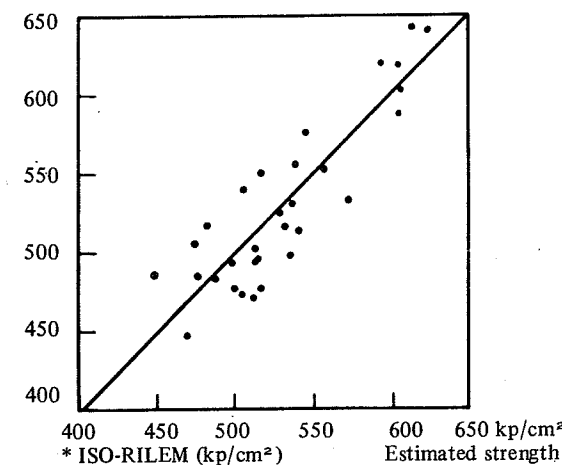
FIGURE 12

$\overline{\sigma} = f$ (Soluble alkalis)

$\overline{\sigma}$ Rilem kp/cm²

$\overline{\overline{K}}_s = (K_2O)_S + 1{,}52 \cdot (Na_2O)_S$

FIGURE 13

Total alkalis (K_2O equivalent):

$$\overline{\overline{K}}_{total} = K_2O + 1{,}52 \times Na_2O$$

Sulphate module (molar ratio): $MSO_3 = \dfrac{SO_3}{0.85 \times \overline{\overline{K}}_{total}}$

The amount of alkali (in K_2O equivalent) present as sulphates (readily water-soluble) can then be calculated by the following terms:

$$\overline{\overline{K}}_s = \begin{cases} 1.176 \times SO_3 & \text{for} \quad MSO_3 \leq 0.5 \\ 0.706 \times SO_3 + 0.2 \times \overline{\overline{K}}_{total} & \text{for} \quad 0.5 \leq MSO_3 \leq 1 \\ 0{,}8 \times \overline{\overline{K}}_{total} & \text{for} \quad MSO_3 \geq 1 \end{cases}$$

The rest of the alkalis will normally be present as constituents of the clinker minerals:

$$\overline{\overline{K}}_{-s} = \overline{\overline{K}}_{total} - \overline{\overline{K}}_s$$

DISCUSSION

Prof J Gillott (University of Calgary, Canada) asked whether, seeing that sulphates were one of the factors responsible for the alkali retention in cement, and that much of the sulphur was derived from the fuel, any thought had been given to the removal of the sulphur from the fuel before it was used to fire the kiln. He mentioned that in Western Canada, which possessed a wealth of oil and natural gas, the sulphur was often removed before the fuel was used resulting in about 20 million tonnes of sulphur currently sitting on the ground.

Mr Svendsen said that this was not done in practice. Development was in fact going in the opposite direction; and the cement industry was expected to burn high sulphur fuel.

Prof U Ludwig (RWTH, Aachen, W. Germany) asked for further information about granule formation, specifically, whether it formed in the burning zone or elsewhere in the kiln, and what the influence of nodule formation on the alkali content of the cement was.

Mr Svendsen said that he did not think there was any quantative information on that point. The main point concerning granules was that in the small wet kilns where granules were formed in the chain system, the dust load was very small and therefore the alkalis tended to condense as individual droplets. They were thus more easily removed from the system than in the dustier kiln systems where the alkalis tended to condense on dust surfaces.

Mr D A St John (DSIR, New Zealand) noted a figure of 900 to 950 kilocalories/kg mentioned in Mr Svendsen's paper. He asked what the energy consumption figures would be without any bypasses.

Mr Svendsen answered that the normal energy consumption of a modern four stage kiln with precalciner was in the region of 750 to 800 kilocalories and each percent of bypass cost approximately 1,5 kilocalories. This meant that with a 100 per cent bypass on this system one had to add another 150 kilocalories on to the normal heat consumption figures, i.e. a total figure of 950 kilocalories/kg (150 plus 800).

Mr Z Limbada (E P Cement Company, Port Elizabeth, South Africa) asked how the volatility of the alkalis would be increased if the burning zone temperature and the duration of time in the burning zone were to be increased. He also asked whether this would affect the equations Mr Svendsen had given and how the parameters were to be taken into consideration.

Mr Svendsen replied that the retention time in the burning zone had always been taken into consideration and that the figures he had given had been measured in practice. He felt that the main factor was the combination of the alkalis and the temperature, i.e. the burnability of the raw mix, not the retention-time, which apparently was less important.