by getting to know something about the mechanism of shrinkage. Secondly, we learnt how to test for shrinkage and how to identify shrinking aggregates rapidly. Thirdly, we discovered to what extent and in what applications we could accept shrinking aggregates in our concrete without jeopardising unduly the life or serviceability of the structure. As testimony to the success of the sound engineering solution I can mention that over half the concrete stone used in Durban today is tillite from the Dwyka Group, vast quantities of sand from the Caledon River near Wepener have been successfully used in much of the concrete in Bloemfontein, and large quantities of sand from the Stormberg Formation of the Karroo were used in the concrete of our famous Orange-Fish tunnel. All these materials fall into the category of shrinking aggregates.

6. CONCLUSIONS

I don't think I am being over-optimistic in predicting that we will achieve the same success with our alkali-aggregate reaction problems as we have with our shrinkage problems, provided we adopt the same pragmatic approach and use the same sound engineering principles in relation to both specification and design of concrete and structures.

Indeed, I would make so bold as to suggest that we in South Africa can be proud of our record. Not only do we have well equipped research laboratories working towards understanding and providing practical solutions to our problems, but suppliers of materials have played a constructive role. For example, cement manufacturers and aggregate producers have arranged seminars on alkali-aggregate reactivity. The cement industry has done its utmost not only to ensure the quality of its product in general, but particularly in the South Western and Eastern Cape where alkali content has been on the high side in the past, every effort has been made to assist the construction industry by significantly reducing alkalis to acceptable levels. Similarly, the suppliers of aggregate have gone to great pains to select better sources of material and to improve the physical characteristics of the aggregate produced.

I have every confidence that the papers and discussions at this conference will stimulate our work on the problem of alkali-aggregate reactivity and bring us closer to a practical solution to the problem.

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S252

ALKALIS IN CLINKER : ORIGIN, CHEMISTRY, EFFECTS

by J Skalny* and W A Klemm*

SYNOPSIS

This introductory paper deals with the role of alkalis in cement manufacture, with emphasis on the alkali-raw feed interactions and their effect on processing parameters and clinker chemistry. Special emphasis is given to the chemistry and mineralogy of the alkali compounds present in clinker because the behaviour of alkali compounds in structural concrete depends to a large degree on their composition, solubility, and other chemical properties. In conclusion, new research data and analytical procedures are discussed.

SAMEVATTING

Hierdie inleidende referaat handel oor die rol van alkalië in die vervaardiging van sement met klem op die alkali-rouvoerwisselwerking en die uitwerking daarvan op parameters vir prosessering en klinkerchemie. Die chemie en mineralogie van die alkali wat in die klinkersteen teenwoordig is word spesiaal beklemtoon aangesien die gedrag van alkali in strukturele beton in 'n groot mate van die samestelling, oplosbaarheid en ander chemiese eienskappe afhang. Ten slotte word nuwe navorsingsdata en analitiese prosedures bespreek.

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Konferensie oor alkali-aggregaatreaksie in beton
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1. INTRODUCTION

The purpose of this introductory lecture is to review the available knowledge on alkalis in Portland cement clinker, with the goal of discussing their origin, chemical nature and reactivity in clinker and their effect on the ultimate performance of concrete. A review of the material presented at past conferences on alkalis in concrete and alkali-aggregate interactions reveals that the majority of work reported addressed the *effects* of the alkali-aggregate reaction rather than its mechanism. This is understandable, as it is primarily the concrete specialist, the contractor, and the structural engineer who first observed and studied the deleterious expansion associated with the reaction.

Reports of damage caused by the alkali-aggregate reaction are still growing and, in our view, will become even more numerous in the future. There are many reasons for this, but the two most important are the increasing use of poorer quality siliceous aggregates and the increasing alkali content of cements.

This discussion will concentrate on the alkalis in Portland cement because it is of the utmost importance to understand that in many areas we will have to learn to live with higher alkali cements or, alternatively, to pay a premium price for low alkali cement. The main reasons for the above fact are economic and result from changing environmental and energy considerations. To improve the efficiency of clinker production in terms of energy consumption and throughput, while simultaneously protecting our environment, cement producers will have to make extensive capital investments. It is estimated that the cost of building a new energy-efficient cement plant will soon reach US $130-140 per ton of yearly clinker production. Any decrease in clinker alkali content by technological change (eg, by using a kiln by-pass system to remove high-alkali dust) increases the operating cost and forces the cement producer to find economical and ecologically sound methods for kiln dust disposal. Because a typical cement producer does not have sufficient economic incentive (eg, premium price) to produce a low-alkali cement, the pressures to continue to use high-alkali cements will increase.

It is certainly time to approach the alkali-aggregate reactivity problem from a more mechanistic rather than descriptive standpoint and, thus, to generate the knowledge needed to *prevent* the deterioration of concrete. This point was emphasized by Diamond[1] in 1975. We believe that the funds required to solve the technical problems of alkali-aggregate reactions and to transfer the knowledge already generated into practice, would be only a small fraction of the funds currently needed to replace concrete damaged by deleterious expansion.

2. ORIGIN OF ALKALIS IN CLINKER

The main source of alkalis in clinker is the siliceous and argillaceous raw materials (eg, clay and marl) used in proportioning raw feeds of suitable composition to form at about 1450 °C the necessary cement clinker minerals. In such raw materials, alkalis are present in the form of finely dispersed aluminosilicate minerals, such as feldspars, micas, illite, etc. Other constituents such as aluminium, iron, magnesium, and fluorine compounds present in these raw materials act as fluxes or mineralizers which interact with a portion of the lime to produce a melt phase, and thereby increase the rate, and decrease the temperature, of tricalcium silicate (C_3S) formation. This compound, together with dicalcium silicate (β - C_2S), is responsible for most of the ultimate properties of concrete.

A smaller portion of the alkalis is introduced with the limestone component or the kiln fuel. Coal-fueled cement kilns in particular are responsible for increased sulphur content and, thus, for the formation of sulphate compounds. The molar ratio of alkali to sulphur is of importance both in clinker formation and in subsequent hydration chemistry, as it dictates the chemical form the alkalis will take. Additional sources of sulphur are the sulphide minerals (eg, pyrite, marcasite) which may be present in limestone, shale, and other raw materials.

3. PYROPROCESSING: FORMATION AND PROPERTIES OF ALKALI COMPOUNDS

Formation of cement clinker from a heterogeneous mixture of ground rocks is a complex process involving high-temperature chemical interactions between solid, liquid and gaseous phases. These interactions include decomposition of clay minerals and limestone, melt formation, diffusion of lime through the melt, C_3S crystallization, and the formation of various alkali compounds. The sequence and rates of these reactions depend on factors such as the composition of the kiln feed and its particle size distribution, the kiln system used, and the sulphur content of the fuel. The chemical composition and final distribution of alkali compounds in clinker follow directly from the raw mix composition and pyroprocessing parameters, such as the heating and cooling rates, gas velocity, and temperature profile of the burning process. Alkali reactions in the kiln feed components begin at temperatures as low as 200 °C during the dehydration and dehydroxylation of clay minerals. As the kiln temperature increases to 1000 °C, ever increasing amounts of alkali are released from parent minerals, form new compounds, melt and volatilize. Since the melting temperature of alkali compounds is typically lower than that of other species present in the kiln feed, they have a pronounced effect on the clinkering process through the formation of new compounds, the overall lowering of melt formation temperature, and possibly a reduction in the rate of free CaO combination.

Alkali-containing compounds that may form during the burning-cooling process and their melting points are summarized in Table 1. In the presence of an excess of SO_3, the most commonly formed compounds are alkali sulphates and double sulphates. When chlorides are present in the raw feed or fuel, alkali chlorides will form and are

TABLE 1 : Common Alkali Compounds in Portland Cement Clinker :

Approximate Melting Temperatures

Compound	Formula	Melting Temperature (°C)
sodium sulphate (thenardite)	Na_2SO_4	884
potassium sulphate (arcanite)	K_2SO_4	1074
calcium sulphate (anhydrite)	$CaSO_4$	approx 1050 (decomposition to CaO + gaseous SO_2 and O_2)
sodium potassium sulphate (ss) (aphthitalite)	$Na_2SO_4 \bullet 3K_2SO_4$	968
calcium potassium sulphate (calcium langbeinite)	$2CaSO_4 \bullet K_2SO_4$	1011
calcium potassium sulphate hydrate (syngenite)	$CaSO_4 \bullet K_2SO_4 \bullet H_2O$	1004 (partial decomposition at lower temperatures)
tricalcium (sodium) aluminate (alkali-doped C_3A)	$NaCa_4Al_3O_9$	1542 C_3A dissociation to liquid + CaO)
dicalcium (potassium) silicate (alkali-doped α - C_2S)	$K_2Ca_{23}Si_{12}O_{48}$	2130 (α - C_2S melt)
potassium chloride (sylvite)	KCl	773
sodium chloride (halite)	NaCl	804

much more easily volatilized than sulphates. It has been generally accepted that, in cases where the molar ratio of $R_2O:SO_3$ is greater than 1,0 and the sulphur present is insufficient to bind all the alkalis in the form of sulphates, alkalis will enter the aluminate and silicate phases to form tricalcium (sodium) aluminate (NC_8A_3) and dicalcium (potassium) silicate ($KC_{23}S_{12}$). In our opinion, the above situation is an oversimplified view of what may occur. For instance, the alkali-doped silicates and aluminates are solid solutions of variable composition, and may form even in clinkers with an excess of SO_3. This is particularly likely when large amounts of SO_3 are derived from kiln combustion gases. The effect of other processing parameters (eg, reducing vs. oxidizing burning conditions) on the form of compounds and the alkali distribution between the clinker minerals is known only superficially.

The ratio of sodium to potassium in cement raw materials and, therefore, in clinker can vary widely. However, in North America and in Europe, there is usually a substantial excess of K_2O over Na_2O. In the presence of sufficient SO_3, a double alkali sulphate (K,Na)SO_4 will form. This substance can range in alkali sulphate ratio, Na_2SO_4:K_2SO_4, from 3:1 to 1:3. The end member of the potassium-rich side is the compound aphthitalite ($Na_2SO_4 \bullet 3K_2SO_4$). Any K_2O present in excess of that required to produce aphthitalite will then form the single sulphate arcanite (K_2SO_4).

The reaction sequence may not end here. With excess SO_3 and the abundance of lime, $CaSO_4$ readily forms above 600 °C. At temperatures of 800 °C and above, K_2SO_4 reacts with $CaSO_4$ to produce a very stable double sulphate, calcium langbeinite ($2CaSO_4 \bullet K_2SO_4$). On the other hand, Na_2SO_4 does not react with $CaSO_4$ to form a double salt, and it further appears that neither do the alkali double sulphates (eg, aphthitalite). Therefore, in an excess of both K_2O and SO_3, calcium langbeinite forms at the expense of K_2SO_4 and not from aphthitalite.

At clinkering temperatures, melts of alkali sulphates and double sulphates are immiscible with the other clinker melt phases. Upon cooling of the clinker, aluminate and ferrite phases solidify at about 1300 °C, but the alkali sulphate phases are liquid to much lower temperatures. The eutectic temperature for calcium langbeinite-calcium sulphate, for example, is 875 °C. As a result, alkali sulphate phases may coat other clinker minerals and are frequently found as incrustations on the surfaces of the silicate crystals (see Figure 1).

An analysis of the major clinker phases for alkali content by Pollitt and Brown[2] has shown that all contain both K_2O and Na_2O in varying amounts. The compound NC_8A_3, a Na_2O-doped C_3A, is the end member of a continuous solid solution series in which Na_2O may be present in any amount up to 7,6 per cent. At the higher Na_2O concentrations, SiO_2 is also required to stabilize the compound. Most clinker C_3A also contains varying amounts of K_2O as a solid solution. However, the compound KC_8A_3 has not been found to exist. The ferrite phase also contains significant amounts of both K_2O and Na_2O.

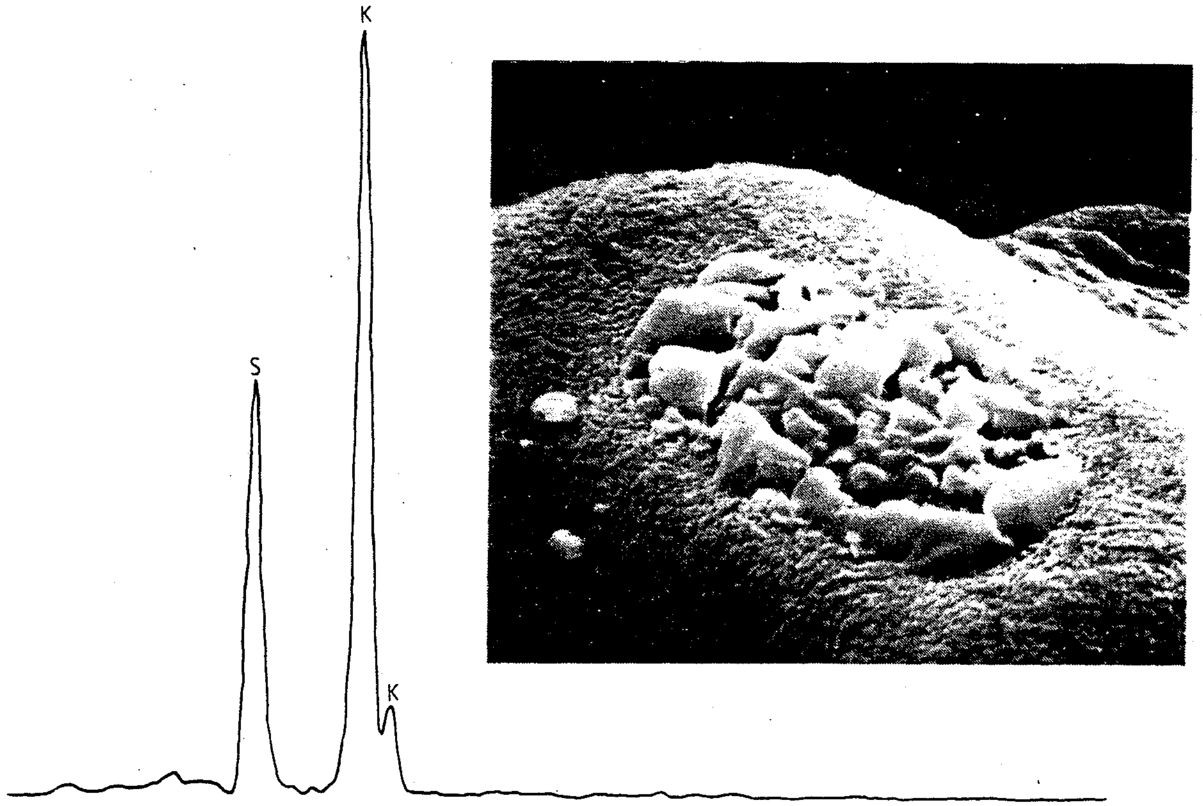

FIGURE 1 : An SEM photomicrograph showing deposits of potassium sulphate on the surface of a C_3S crystal (x 3600), with below it an EDS analysis of the deposit showing the composition of sulphur and pottassium.

The silicate minerals C_3S and C_2S have been found to contain both K_2O and Na_2O. Midgley[3] found that in industrial clinkers, alkalis tend to be found in somewhat greater concentrations in C_2S than in C_3S, and at the highest levels of K_2O, the α - C_2S polymorph is stabilized and the composition approximates $KC_{23}S_{12}$. Where C_2S and C_3S are found together as co-existing phases in cement clinker, the relative amounts of alkalis were determined to establish the degree of partitioning between the two silicate phases. In the case of Na_2O, the partition coefficient $C_2S/C_3S \approx 3$, whereas for K_2O, $C_2S/C_3S \approx 7$. The average molar alkali content of C_2S was found to be Na_2O = 0,008 and K_2O = 0,008. In general, K_2O and Na_2O are interchangeable in the aluminate, ferrite and silicate phases and, we believe, their relative amounts are dependent also on the actual quantities present, rather than on any special affinity of aluminates for Na_2O or silicates for K_2O.

Because of the relatively high volatility of the alkalis, especially K_2O, a circulating alkali cycle is formed inside the kiln. The volatilized alkalis, carried by the combustion gases, condense on the cooler kiln feed particles and are carried back into the burning zone where they again volatilize. This cycle causes particular problems in modern efficient preheater kilns. As the concentration of alkalis in this internal cycle increases, larger quantities are discharged with the clinker. To avoid this excessive increase of alkali concentration in the clinker, some kiln systems (eg, with four-stage preheaters) have to be equipped with bypasses which divert a portion of the high-alkali gases from the kiln to a dust collection system. The use of a bypass has a negative influence on the heat economy, in that each 1 per cent of bypassed gas volume increases the energy consumption by 4 - 5 kcal/kg of clinker. Each 10 per cent of bypassed gas volume also removes approximately 1 per cent of the raw feed in the form of an alkali-rich kiln dust[4].

Although present in relatively small amounts, alkalis influence the clinker formation by changing the composition and temperature of melt needed for the rapid formation of C_3S. Greene and Bogue[5] have shown, for example, that NC_8A_3 solidifies from the interstitial melt phase at about 1440 °C, which can significantly reduce the quantity of clinker liquid required for adequate burnability of high-alkali clinkers. Furthermore, lime reacts more slowly with $KC_{23}S_{12}$ than with C_2S in order to form C_3S. As 1 per cent of K_2O may lead to 20 per cent of $KC_{23}S_{12}$, this then results in an increased free CaO content, a decrease in the burnability, and possibly changes in the rate and the mode of cement-water interaction. Additionally, this produces changes in the optimum gypsum content, an area not very well explored but of the utmost importance.

TABLE 2 : Solubilities of Some Alkali Salts

	Solubility (grams salt / 100 g H_2O)	
Compound	25 °C	75 °C
NaC1	35.6	37.8
KC1	37.0	49.7
Na_2SO_4	27.9	43.4
K_2SO_4	12.0	20.8
Na_2CO_3	29.4	45.4
K_2CO_3	112.1	136.4
$CaSO_4 \cdot K_2SO_4 \cdot H_2O$	0.25	-
$Na_2SO_4 \cdot 3K_2SO_4$	similar to K_2SO_4	--
$2CaSO_4 \cdot K_2SO_4$	similar to $CaSO_4$	--
$CaSO_4$ (sol.)	0.63	0.27
$CaSO_4 \cdot 0.5H_2O$	0.71	0.29
$CaSO_4 \cdot 2H_2O$	0.21	0.18

There is inadequate knowledge of the effects of the alkali compounds present in the clinker on cement hydration behavior. This is especially true with respect to the relative solubilities of the simple versus the more complex compounds (Table 2). Interactions within the hydrating aqueous medium are unclear, but it seems possible that K_2SO_4, initially rapidly dissolved, can react with $CaSO_4$ and recrystallise as the double salt hydrate, syngenite. Calcium langbeinite probably also hydrates to form syngenite. However, the fact that the volatile alkali sulphates condensed on the surfaces of the major clinker minerals would also make them available to dissolve in the very early stages of cement hydration. The relative rates of hydration of β - C_2S versus $KC_{23}S_{12}$ and C_3A versus NC_8A_3 are largely unexplored, and the limited literature data are controversial.

Depending upon the conditions of cement grinding or storage, free K_2SO_4 in the clinker may react with moisture and gypsum to form the double salt syngenite ($CaSO_4 \cdot K_2SO_4 \cdot H_2O$). Syngenite generally forms during adverse cement storage conditions and gives rise to pack-set and flowability problems (see Figure 2). However, Kurdowski[8] has found that it can be rapidly formed during the grinding of clinker with gypsum in an open circuit finish mill with water injection. Syngenite is poorly soluble, but reacts with C_3A, in a similar way to gypsum, to form ettringite. At this point, the K_2O is again released to the solution.

4 EFFECT OF ALKALIS ON CEMENT PROPERTIES

We will not discuss in detail all of the effects alkalis have on the mechanical properties of concrete. These are reviewed elsewhere [7],[8]. Rather, we will concentrate on what chemical aspects *cause* the physical changes observed. Also, we will not discuss the alkali-aggregate reactions, because we expect these to be discussed by other participants.

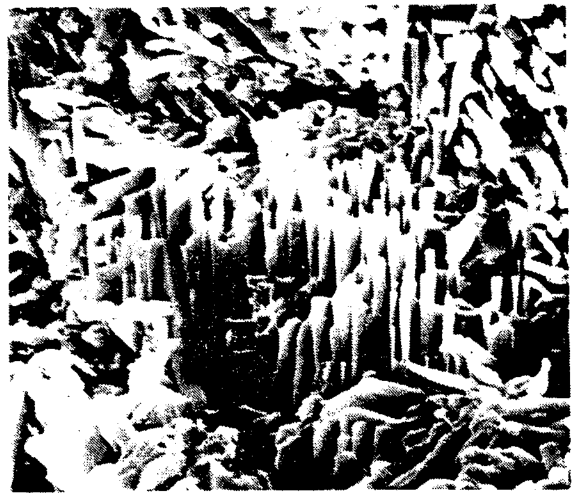
FIGURE 2 : An SEM photomicrograph of syngenite $CaSO_4 \cdot K_2SO_4 \cdot H_2O$) formed during clinker storage (x 3000)

The ultimate technical goal of cement and concrete producers is a strong and durable structure. In order to give these properties to a concrete structure, the cement has to react with water, often in the presence of chemically active admixtures, to form new compounds having the ability to fill the available pore spaces. These hydrated compounds will serve to bind the sand and aggregate particles together, resist environmental influences (eg, temperature changes, reactive solutions), and produce a solid with a stable volume. The reactions by which this is achieved are complex, reflecting the complex composition of cements. The most important reactions occur within the first few hours of cement-water interaction, when the exchange of ionic species is not inhibited by the solidification of the system occurring as a consequence of these reactions. The reactions occurring in the liquid phase and on the solid-liquid interface control not only the setting phenomena but also the conditions under which the mechanical properties develop or deteriorate in the subsequently solidified system. In other words, to control the ultimate properties and stability of concrete, it is imperative to control the early hydration reactions. This can be accomplished by modifying the reaction conditions (eg, curing temperature), introducing additional system components (eg, admixtures, fly ash), or using different types of cement or different mix proportions. Control of the ultimate concrete properties would be much extended if we were able to measure, influence and control the rates, sequences and modes of reactions needed to form the hydrated cement paste matrix. Specifically, the phenomena we need to modify in order to extend our control of concrete are the relative dissolution rates in pore solutions of various clinker minerals. These minerals differ in crystal structure, reactivity and distribution of minor elements, and result in the formation of hydrated species in a certain sequence and at a specific rate.

In all these phenomena alkalis play a crucial role. As has been shown by Diamond[1], McCoy[9] and others, alkalis in the aqueous liquid phase (pore solutions) strongly affect the rates, sequences of reactions, and the structure development. By changing the relative solubilities of calcium, silica and other species, they may modify the interactions with admixtures, change the morphology and surface area of hydrates formed, influence the cement paste-to-aggregate bond and the distribution of air voids, and change the solubility (and thus the durability) of the hydrates that form the composite matrix.

Hydration of cement does not proceed in a simple lime-saturated solution, but in a solution saturated with both lime and alkali. It is important to realize this fact when trying to reproduce field phenomena in the laboratory. The concentration of alkalis in the pore solution may vary from as low as 0,3 M to as high as 0,7 M. It is also important to take into consideration the anions present in the system. For example, Na_2CO_3 will influence the liquid phase in a way different to that of Na_2SO_4, because CO_3^{--} and SO_4^{--} have a different effect on the solubility and hydration of clinker minerals present in the system. Both, however, are found to accelerate the early silicate hydration reactions. NaF, on the other hand, is a strong retarder. Studies performed on pure clinker minerals cannot be directly correlated with cement, mortar, or concrete because of the changes in relative solubility caused by factors such as the other species present, the mixing procedure, and the heat evolution.

Alkali sulphates accelerate cement hydration and early strength development primarily by affecting the C_3S hydration. They influence $Ca(OH)_2$ solubility, decrease the activation energy of C_3S dissolution or hydration, and prevent the poisoning of C_3S hydration by alumina from the C_3A. All of these and other phenomena may have an influence at the same time. Although the optimum gypsum content is known to relate primarily to the cement fineness and C_3A content, the effect of alkali sulphates – especially in view of increasing clinker alkali content – should be re-evaluated [10].

The effects of soluble alkalis on the rate of early cement hydration and on the subsequent strength development is well known. Whereas alkali sulphates accelerate the hydration process to produce higher early strengths, it has been found that the later strength may decrease somewhat. This issue was discussed recently by Osbaeck[11] who reported that the highest correlation coefficient between a strength parameter and a compositional parameter exists between the 28-day strength and the quantity of soluble alkali. No correlation was found between strength and the non-sulphate bound alkali. The same study also showed an increase in 1 and 3-day strength, and a decrease in 28-day strength.

Data by Johansen[12] revealed an inverse relationship between the amount of combined water after 3 minutes of hydration and the 28-day strength. This implies that the reason for the negative effect of soluble alkalis on later strength development is the increasing reaction rates at very early hydration stages. A mechanistic explanation of this finding was not made. The rate of alkali release has important implications with respect to the alkali-silica reaction as it may control the alkali and hydroxide concentrations in the pore solution and, thus, the time of formation and the alkali-silica ratio of the reaction products.

McCoy[9,13] found that, depending upon the total alkali content and the alkali:sulphate ratio in cement, the water soluble alkali content, determined by a 10-minute aqueous extraction procedure, varied from 10 per cent to over 60 per cent of the total alkalis present. This 'soluble' alkali content actually showed a better correlation to the degree of alkali-aggregate reaction than the total alkali content.

Normal setting of cement is controlled by the hydration of C_3S. However, when excessive amounts of minor compounds (eg, alkalis) are present, the relative solubilities in mixing water of the clinker minerals and calcium sulphate may change and, thus, the control of setting becomes dependent on the relative availability in solution of aluminates and sulphates. A similar situation can occur in the presence of admixtures. Disproportionate amounts of aluminates and sulphates in the liquid phase may lead to early stiffening, false set, flash set, increased slump loss, etc. This has been confirmed in recent work by Locher et al.[14], who investigated the relationship between C_3A reactivity and sulphate availability in the course of initial hydration reactions and their effect on setting.

An example of the effect of alkali compounds on the behaviour of cement was recently given by Tang[15]. His data show that syngenite, on an equal sulphate molar basis, retards C_3A hydration to a larger extent than gypsum. However, syngenite as well as calcium langbeinite seem to accelerate the calcium silicate hydration – a finding consistent with the known effect of gypsum on C_3S hydration. Tang also reports that the optimum SO_3 content, when added in the form of syngenite or calcium langbeinite is only about half the amount added as gypsum. The importance of the relative reactivity (solubility) of aluminates and alkali sulphates on setting and workability was reported by Sprung[16].

There are two additional concrete properties which, in our view, may be strongly influenced by alkalis – they are the volume stability and the cement paste-to-aggregate bond. Alkalis are known to be able to enter the structure of C-S-H, thus changing its composition, morphology and, most probably, also its behaviour during drying and rewetting. Unfortunately, almost no information is available on the subject. Preliminary results obtained in this laboratory [17] indicate that the rate of drying shrinkage of concrete is somewhat reduced by the addition of 2 per cent K_2SO_4, by mass to cement.

The paste-to-aggregate bond is strongly dependent on the composition of the liquid phase at the paste-aggregate interface. It is our belief that higher cement alkali content, leading to increased pH and changes in the rate of dissolution of clinker components, may lead to differences in the 'quality' of the paste-to-aggregate bond, a property not very well explored [18].

5. ANALYTICAL IMPLICATIONS

Analysis of alkali distribution in cement clinker is not an easy task. However, the distribution of potassium and sodium among the various clinker minerals has important implications as to their rate of dissolution when the cement is eventually mixed with water. The dissolution rates affect the early hydration reactions and, in the present authors' view, may also influence the composition of the pore solutions in mature stages of hydration. This can directly affect the durability of concrete.

Bogue-type equations are available for calculating the approximate composition of alkali compounds in Portland cement clinker [19]. It has been assumed that the alkalis will first react with SO_3 in the raw feed to form the alkali sulphates, K_2SO_4 and Na_2SO_4. Alkalis present in excess of the available SO_3 will react with other substances present to form $KC_{23}S_{12}$ and NC_8A_3.

However, this is a simplistic view and, as we have shown earlier, is not altogether correct. It is now possible by several analytical techniques to semiquantitatively determine the actual alkali contents in C_3S, C_2S, C_3A, and Fss, as well as isolate and determine the quantities of separate alkali phases such as sulphates and double sulphates. Pollitt and Brown[2] have described selective dissolution techniques in which the alkali contents of clinker phases are progressively determined. Ground clinker is first extracted with water to remove all alkali sulphates and double sulphates. Next, the silicate minerals (C_2S and C_3S) are removed from this residue by dissolution in a solution of salicylic acid in methanol. The residue from this step consists entirely of the interstitial clinker phases (C_3A and Fss) plus any MgO or $CaSO_4$ which was also present in the clinker. Finally, the ferrite phase is isolated by dissolving the other phases, including aluminates, in an aqueous acetic acid solution at pH 3,5 to 3,8. At each step of the process, the residues were analyzed for alkali content. Compound identifications were made by X-ray diffraction. In the case of silicate minerals, no separation could be made. However, Midgley[3] has determined the minor element contents of both C_3S and C_2S in clinkers by electron microprobe analysis. The analysis of co-existing C_3S and C_2S particles has also made it possible to estimate the partitioning of alkalis between the two silicates during clinker formation.

Upon hydration of the cement, the alkali sulphates and double sulphates are rapidly dissolved in the aqueous phase, whereas alkalis present in the aluminate, ferrite, and silicate phases are released more slowly over a period of days or even weeks and months. These alkalis are retained in pore solutions within the hydrating paste body where they may either enter the hydration product structure as it is formed or be available for other reactions such as with reactive aggregate. Estimates of the amounts of such alkalis in the early stages of hydration can be made by mechanically compressing the hydrating paste in a steel piston and die filtration apparatus which allows the pore solution to be squeezed out of the paste under high pressure. Such techniques were employed, for example, by Diamond and Barneyback[20]. The pore solution can then be immediately diluted and analyzed by the appropriate means such as atomic absorption spectrophotometry.

The above discussion of some of the available analytical methods touches on the two problems we are facing. First, we do not have a perfect method for phase separation, especially in hydrated systems. Inadequate separation of phases makes the results of alkali analysis questionable. On the other hand, analysis of multi-component systems by a combination of electron microscopy with microprobe or energy dispersive spectroscopy has its limitations in the inadequate accuracy of these methods in analyzing for light elements. Development of better selective dissolution and separation techniques, and improvement of the accuracy of spectrophotometric or other methods of alkali analysis are among the analytical challenges to be solved.

6. CONCLUSIONS

Changes in pyroprocessing technology and the use of coal as the primary fuel in clinker burning has resulted in renewed interest in the content and form of alkalis in cement, and in the possible effects which alkalis may have on concrete.

Alkalis, mostly present in the form of sulphates, do have a pronounced effect on the rate and sequence of certain reactions during clinker production by influencing the temperature of melt formation as well as its viscosity and surface tension. Because of their relatively low melting point, alkalis remain fluid below the solidification points of other clinker phases and then crystallize in the form of highly soluble sulphates on the surfaces of the major clinker minerals formed.

Upon contact with water, the alkali sulphates rapidly dissolve and influence the reaction processes by changing the solution pH and the solubilities of other clinker minerals. Solid products of hydration incorporate alkalis in their structures. This may result in compositional and morphological changes which, in turn, influence the physical properties of fresh and hardened concrete. In particular, the presence of alkalis in the cement paste pore solution may lead to abnormal setting phenomena, decreased strength, and reactions with siliceous aggregate.

Production of quality concrete with high-alkali cement is possible. However, more knowledge should be generated to enable a proper selection of concrete components, mix design proportions, and curing procedures to be made. In particular, more knowledge is needed on the basic chemical interactions of alkalis with clinker components, and on their effect on the morphology and physical properties of the hydrates.

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DISCUSSION

Prof U Ludwig (RWTH, Aachen, West Germany) asked at what stage the alkali-bearing C_2S was formed. The paper only gave the information that it formed at a relatively high concentration of alkalis and only after other alkali compounds had formed. However, it was known that C_2S formed fairly early in the clinkering process.

Dr Skalny repeated that the model was oversimplified and that these reactions would only occur if clinker were to be burned at equilibrium conditions, which was not done. As the exact sequence was not known it was entirely possible that under some conditions C_2S formed first which he claimed had formed at a later stage.

Prof Ludwig gave it as his opinion that this alkali could be set free at 900 °C and that C_2S formation took place at the same temperature. The paper showed an SEM photomicrograph with potassium sulphate deposited on the surface of a C_3S crystal. He therefore asked where the potassium sulphate originated from since the C_3S was formed above 1 200 °C.

Dr Skalny replied that potassium sulphate had a low melting point and therefore, as the clinker began to cool, was deposited onto its surface where it was readily detectable. This deposition already took place in the high burning zone while it was still circulating.

Mr E H J van Rensburg (Murray & Roberts, Cape Town) asked if the solubility of the alkali compounds could be the elusive factor in the reaction mechanism Dr Davis had referred to. In his keynote address he had mentioned cases in which reactive aggregates used with high alkali cement had not given the expected expansion.

Dr Skalny stressed the fact that alkalis were assessed as being either total acid soluble or water soluble. Different experimental conditions affected the rate of solubility of the water soluble alkalis. Although the alkali sulphates were more soluble than the calcium sulphates, it had not been established how the variation in experimental conditions influenced the difference between them. He had listed the solubilities of some of the alkali salts in water. However, in a complex hydrating system such as Portland cement, these solubilities were still unknown.

Prof S Diamond (Purdue University, USA) referred to his work in expressing pore solutions from hardened mortars and cement pastes. He had recently become interested in this field, and had attempted to analyse pore solutions from various cements, as soon after mixing as possible, usually 10 to 15 minutes. His findings were that regardless of how early the actual mix solution was separated from the cement, much of the alkali, particularly that fraction which was associated with the alkali sulphates, was already in the mix water pore solution. This indicated that the soluble components were in fact, even under realistic mix conditions, almost instantaneously dissolved. He felt that variations in the rate at which alkalis were transferred to the mix water distinguished only between the soluble components (which for all practical purposes dissolve instantaneously) and those alkali components coming primarily from the clinker minerals which will take considerably more time to dissolve. Thus there was no gradation in his opinion; the substance was either instantly soluble or took a long time to dissolve.

Dr Skalny commented that once the alkalis were dissolved they did influence the way in which the other clinker minerals hydrated. However, it was not known whether some of these alkalis were eventually picked up by the hydration products, or when and how, so that it was possible that in the presence of alkalis the rate of reaction of the various clinker minerals changed and that some of the alkalis were being used up and therefore were not available later for deleterious expansion.

Dr P Grattan-Bellew (NRC, Ottawa, Canada) said there was an extensive body of literature relating to the investigation of the relation between the expansivity of aggregates and the solubility of the alkalis. When measured by ASTM Method C114 in which they were placed in water for an hour results had correlated very poorly with observed expansion. He felt the cause of this might be that the one hour solubility was too short despite Prof Diamond's finding that the alkali came into solution instantaneously. He suggested that if the water solubility were to be measured over a longer period, the results might correlate better.