Clive Rogers

THE EFFECT OF ALKALIES ON THE PROPERTIES OF CONCRETE

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FOREWORD

The papers in this book were presented at a Symposium held at the Cement and Concrete Association, Wexham Springs, between the 6th and 9th of September 1976. This meeting followed similar Symposia held in Denmark, 1974 and Iceland, 1975. The organising committee of the London Symposium were most fortunate in being able to welcome leading experts from many parts of the World to this meeting. In the space of a single year a surprising wealth of new information and ideas has become available providing the tangible evidence of flourishing research in this field of study and the substance of this present volume. The papers have not been assembled in the precise order of original presentation but have been grouped into six sections reflecting the various aspects of the subject studied. The boundaries of the sections should be gradational since some of the papers might equally appear under several headings. However, it is hoped that the groupings chosen will provide some guidance to the reader and that the papers themselves will stimulate the interest and further researches necessary for the full understanding of the effect of alkalies on the properties of concretes.

A. B. Poole
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1. INTRODUCTION

THE EFFECT OF ALKALIES ON THE PROPERTIES OF CONCRETE

THE OPENING ADDRESS TO DELEGATES ATTENDING THE 1976 SYMPOSIUM

given by

DR. G. M. IDORN

Aalborg Portland Research and Development
Denmark

Dr. Sharp, Ladies and Gentlemen,
My dear Friends,

It is a great pleasure to introduce and to chair the first session of the

Third International Meeting on the Effects of Alkalies on
the Properties of Concrete at C&CA, Fulmer Grange.

Each of the two preceeding meetings, Køge 1974 (1), and Reykjavik 1975 (2), have been special in their character and arrangements. This one will be second to none in its own right and ways.

The preparatory work is so promising of success that failure is only to be expected if those attending are passive or do not present qualified contributions. And this is not to be feared.

Once upon a time a famous Danish storyteller wrote a fairy-tale called

The Ugly Duckling.

It lived under great stress in a hostile environment, superficially condemned by the community for possessing inferior beauty and virtues. By a lucky opportunity the Duckling's underlying qualifications were revealed and became acknowledged.

I do not think that the broadening of the scope of this third meeting relative to the two preceeding ones will *in itself* cause the reputation of alkalies in concrete to change from an »Ugly-Duckling» ignorance and fear-conditioned condemnation like bad and evil constituents of cement, to a »Young Swan» recognition of their true nature and usefulness in cement and concrete technology. Solidly established misconcepts and opinions do not change that easily.

When a few of us initiated this series of meetings some years ago, we felt that more exchange of newer knowledge between those actively engaged in research regarding the nature of alkalies in cement and concrete, would be beneficial.

We also thought that an arrangement of a broader meeting like the typical formal symposia, supported by international organisations and with representative presentations involved, would probably not become successful. We feared — or let me put this judgement upon myself — I feared that such an arrangement might even inflict damage and reinforced misconcepts on the further progress of the research, we deal with and care for, because we did not have any sufficiently new knowledge on alkali-silica reaction available and were not apt for presentation so as to meet the demand from our users of new knowledge:

The industries concerned
Engineering practice
Authorities

We did assume that the need for new knowledge was likely to increase soon due to the general economic development and rationalisation efforts in our industries, and also in view of the increasing pressure on the availability of the resources, especially in the most industrialized countries.

We did see it as a risk that this demand might soon cause practice to adjust cement and concrete technology from fear of alkali-silica reaction without considering newer knowledge or asking for help from new research — and that would be neither economical nor progressive in the further development.

Since then, the perspectives for the energy and the materials' resource demand, and also the economy of cement and concrete manufacture and utilization, have confirmed our views regarding the need for more knowledge, and fortunately our meetings are at the same time revealing that a considerable growth and improved status of the research concerned have occurred.

We know much better than 3 years ago in which areas more understanding of the nature of alkali-silica reactions is still required, and »how to go for it».

However, concurrently, we must realize that views and opinions regarding the effects of alkalies in general tend to become more conflicting than before.

This is due to both the steadily increasing concern about the availability and the costs of suitable aggregates in many countries and to urbanization and industrialisation in areas with practically unexploited and unknown aggregate resources and with low levels of technical education, and also to the urgency for reducing expenses and energy consumption in cement manufacture. Influential are also the increasing public requirements for precautions against pollution of air, soils, and water, and the engineering drive towards improved utility of materials and design in construction practice and in housing, without exceeding reasonable safety regulations.

This is why research becomes increasingly exposed to conflicting demands for specific assistance and service regarding alkalies in cement and concrete.

Unfortunately, the need for general, underlying scientific research in its own right — to create more knowledge — carries less weight than in the past, both in the society and in industries, yes, even in the formalized international research cooperation.

And this again is why enthusiastic dedication is required on the part of the researchers to make the »Ugly-Duckling» misconcept of alkalies in cement and concrete change into realistic approaches and fruitful communication about the true nature and extent of the problems.

That can only be achieved by establishing the relevant knowledge on alkalies all along their pathway: as constituents of the cement materials, as influential during the cement manufacturing processes and the concrete making, and in the end as »bacteria» causing chemical reactions in hardened concrete under certain conditions, and thus adversely affecting the durability of structures, houses, etc.

Such a comprehensive and coherent disclosure of the nature and effects of alkalies is what the programme committee for this meeting has invited the participants to commence.

The papers announced for presentation show that the importance of this approach is appreciated.

Nevertheless, we must acknowledge that there are colleagues in production and sales departments of cement and concrete industries who think that the most advantageous situation exists, if no one becomes aware of »alkali-problems», so that national and international concern would remain entirely avoided. Such attitudes can only be explained by saying that research has not yet done its job properly. — The communication to colleagues and business operators has not yet become effective. In other words, the value of *knowledge* has not been sold to the users of research.

Let us therefore consider what makes the cement consumers concerned about alkalies, since they constitute the most numerous among the customers of our research, and they manage by far most of the invested capital in the cement and concrete business sector.

A few figures may illuminate the present situation. The annual cement sales are:

In Denmark	0.1	Bill.	dol.
- USA	4.0	-	-
- the World	35.0	-	-

whereas the annual »sales» of concrete can be estimated as follows:

In Denmark	0.5 — 0.8	Bill.	dol.
- USA	25 — 30	-	-
- the World	200 — 300	-	-

The research on alkalies in cement and concrete has a true global interest and applicability. Accordingly, there is a demand for this research represented by an annual sales-value of 200 — 300 Bill. dol. from cement consumption enterprises, against 35 Bill. dol. from cement manufacturing business.

Which is then the cement consumers' request on service from our research:

First, the cement consumers have a certain knowledge about the influence of the alkalies on the strength development of concrete. Therefore, research is requested to offer more guidelines for an improved utilization of this dependance. However, beyond the strength specifications based upon which the consumer buys his cement, and pays for its properties, there is real profit to gain from strength/alkali dependance only for a minority of cement consumers, namely those operating accurately monitored industrial cement product manufacture. In normal engineering practice so many factors other than the alkali contents — and much easier to adjust — are decisive for the strength development, so that the alkali contents is a useless measure as a controlling parameter in practice, and this is even more the case in handcraft dominated concrete making.

This is also the reason why the cement consumers so easily preserve the picture of alkalies in cement and concrete as predominantly associated with deterioration, or as it has been said: Alkali-silica reaction is a type of concrete cancer, in which the alkalies from the cement and the silica from reactive aggregates act as the virus.

This 200 to 300 Bill. dol./year concern on the part of the cement consumers cannot be disregarded by research. Neither can we serve the consumers by enabling removal of alkalies from cement or by restricting aggregate acceptance to innocuous materials only, to secure durable rentability of these investments. This is not feasible, and therefore research must also consider the cement and aggregate producers' problems.

There are for instance often good reasons for maintaining high alkali contents in cement deriving from the nature of the raw materials, the economy of kiln operations and investments, the »clean air, water and ground» policies and the increasing restrictions on the aggregate resource utilization.

None of us here can believe that there are other ways out of these dilemmae than what can be established through new knowledge which is sufficient to secure:

1. Reasonable engineering compromises at the present stages of cement and concrete technology, and
2. Future development of technologies which aims at reducing costs to be imposed on concrete by restrictive precautions or failures caused by neglectance of precautions.

Let us at last look at the problems as viewed from the side of the authorities, upon whom the society inflicts more or less unspecified general responsibility for:

1. Reduction of energy and materials resource consumption, and planning of the overall national or regional development,
2. Reduction of pollution and, alternatively, utilization of waste products, and
3. Economy of public engineering works — more than often as incompatible demands on minimum initial expenses and maximum service lifetime at lowest possible maintenance expense levels.

It is easy to see that these different positions of immediate responsibilities may well create all kinds of *apparently* conflicting views and interests, if everybody concerned is evaluating and deciding on a cate-to-case basis, and also very different evaluations as far as planning for long-term investments and development is concerned.

One must also be aware *that* the authorities as the overall political controllers do not themselves invest in the manufacturing crafts and industries, *that* the cement manufacturers are predominantly locked for long periods to given manufacturing technologies, and *that* the cement consumers who possess most of the technology flexibility generally speaking have the least capability available for exploitation of their development potentials.

Because of this very complex and fragmented technology/economy/responsibility background, the research (which annually comprises only microscopic efforts in relation both to cement production and cement consumption investments) has not yet been able to remove the »Ugly-Duckling» policies which one or the other partner in the cement and concrete enterprises still often chooses as a defensive position.

This is why the core of dedicated exchange of background and applicable knowledge and ideas to be presented at this meeting is so important as a nucleus for the creation of a broader progressive environment — to the benefit and economic advantage for all parties involved.

During our series of meetings the growth of a collegial sense of forming part of a multitude for the promotion of valid knowledge creation is one remarkable achievement.

But more pragmatically seen: the results and the markedly increasing intensity of new matters presented in the contributions prove the benefit/cost ratio of these gatherings to be very satisfactory.

Thus, also from a cooperative and a research rentability viewpoint I have great confidence in the output of this third meeting.

As a conclusion I should like to thank a high officer of an organisation of true authority — the ASTM —, namely Mr. Bryant Mather, and an American, public sponsor of international research cooperation — the European Research Office of the US Army Corps of Engineers — represented by Mr. Hoyt Lemons, for having so strongly supported our arrangements, each in his way.

I feel convinced that their confidence will be duly repaid in that with the added value of the two preceeding meetings we can begin to see a way to compile and present much needed information from our research workshops to our customers: industries, consumers, the public.

I should very much like a forthcoming meeting to deal also with these aspects of our topics.

With thanks to C&CA and Queen Mary College for the arrangement of facilities and programme etc. I am pleased to open the first session of our conference.

G. M. Idorn

Literature:

(1) Aalborg Portland R&D Seminar on Alkali-Silica Reaction, Hotel Hvide Hus Køge, Denmark, 20-21 May, 1974, presented by AP-R&D

(2) Symposium on Alkali-Aggregate Reaction
Preventive Measures
Reykjavik, August 1975,
Iceland
Rannsoknastofnun Byggingaridnadarins

ALKALIES IN CEMENT & CONCRETE

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Read by Ms A.E. Moore

ABSTRACT

Varying degrees of importance have been assigned to the effects of alkalies on a wide variety of cement and concrete characteristics. In some areas, notably in the United States, low alkali cements have come to be more favourably regarded than high alkali cements, while in other areas there is no comparable preference for low alkali cements. Such differences, however, suggest that there is a need to examine the behaviour of alkali in cement and concrete.

The presence of small amounts of alkalies may modify the compound composition of clinker and affect its behaviour while alkali compounds, which greatly exceed the solubility of other clinker compounds, may affect the physical properties and hydration characteristics of cement paste. Under appropriate exposure conditions, alkali may contribute to diverse phenomena such as surface staining, efflorescence, scaling and siliceous aggregate reaction and expansion in concrete. Despite the detrimental effects attributed to alkali , the general performance properties of cement can be suitably maintained provided raw material variations are anticipated and minimized and due attention is given to burning clinker, and to the fineness and gypsum content of cement.

Introduction

Alkali metal compounds are minor constituents of portland cement. They are both readily and rapidly soluble in water. They may affect the behaviour and properties of both freshly-mixed and hardened cement paste and concrete and may contribute to the incidence of several problems which develop slowly in concrete.

All of the relevant characteristics of a cement are seldom identified or completely defined. The observed functions and performances of cement paste and concrete, on which experimental conclusions are based, may be influenced by many different interactions but are generally attributed to a relatively few factors such as compound compositions computed from chemical analyses and surface area measurements. However, other more significant characteristics are rarely stated. Examples of these deficiencies concern the actual compound compositions, crystallinity, heat treatment and production conditions of clinker, fineness characteristics such as particle size distribution, distribution skewness and particle shape of both clinker and gypsum, and the surface condition of particles when mixing with water commences. All of these factors are highly significant and may influence water requirement, setting time, stiffening tendencies, strength development, shrinkage and the sensitivity of cement to react with admixtures.

The present paper sets out to discuss the occurrence and behaviour of alkalies in cement and concrete, to indicate the effects of alkalies in cement reactions and in various phenomena which occur in freshly-mixed and hardened cement paste and concrete, and to comment on procedures that may be used to reduce the alkali content of cement and to modify some of the adverse effects produced by alkalies in concrete.

Alkalies in Clinker

Alkali compounds in concrete are derived principally from cement, with aggregate and water as minor contributors, and from secondary external sources such as ground-water and air-borne spray. The common alkali metal ions, sodium and potassium, are present in variable but minor amounts in clinker generally within the range 0.1 - 1.5% $Na_2O + K_2O$. They are generally derived from the argillaceous fraction (clay or shale) of the raw meal or from coal ash. Other fuels may also indirectly affect the composition of clinker. Residual fuel oil usually contains large amounts of sulphur, while natural gas contains neither alkalies nor sulphur compounds. The amount of sulphate in clinker affects not only the mode of occurrence of alkalies, but also the amounts of some of the other clinker compounds.

Newkirk (1951,1952)[6,7] has discussed alkali-clinker systems and described the occurrence of alkali phases and accompanying compound compositional changes in clinker. Alkalies combine preferentially with sulphate to form a solid solution of roughly constant composition, and consisting of potassium sulphate and sodium sulphate in an approximate 3:1 molecular ratio. Alkalies, in excess of the amounts combined with sulphate, combine with dicalcium silicate (C_2S) to form the compound $KC_{23}S_{12}$ and with tricalcium aluminate (C_3A) to form the compound NC_8A_3, and may adventitiously occur in solid solutions with clinker compounds or as a constituent of glass. The amount of sulphate ion derived from raw meal and fuel therefore affects the phase composition of the clinker. When the amount of sulphate ion is large and when the amounts of alkali ions are small, alkalies are present largely as sulphates. When the sulphate ion is deficient, the compounds $KC_{23}S_{12}$ and NC_8A_3 together with the potassium sulphate-sodium sulphate solid solution occur in variable amounts. With increasing amounts of alkali ions, the amounts of the compounds $KC_{23}S_{12}$ and NC_8A_3 increase and calcium oxide is displaced from dicalcium silicate and tricalcium aluminate. Since the amount of C_2S which is available to combine with the calcium oxide to form C_3S is rapidly depleted, free calcium oxide becomes an equilibrium phase in clinker. It is clear that changes in the chemical composition of raw meal, of raw materials and of fuels can have marked effects on the compound composition of clinker and consequently can influence cement behaviour. Moreover, since the clinkering reactions in kilns do not always reach their expected equilibria.the amounts of the different compounds formed may differ markedly from those computed from the oxide analysis. The presence of other negative ions and variations in raw meal characteristics, in burning temperatures, in fuel combustion and in kiln operating conditions can also affect the alkali content and compound composition of clinker. Provided these variations are anticipated and suitable action is adopted to counter or minimize their effects, clinker and cement possessing satisfactory quality and properties can be produced.

Approximately 50% of the alkalies in raw meal and coal ash may be volatilized during burning, and much of this alkali is re-deposited in the chain section of the kiln, and in pre-heaters, dust precipitators and filters. The practice of re-circulating re-claimed precipitated dust to the kiln generally changes the raw meal composition adversely and increases the alkali content of clinker. The burning of high sulphur fuel oil in place of coal tends to increase the sulphate content of clinker and, depending on burning conditions, may reduce the amount of alkalies that are volatilized and thus affect the compound composition of the clinker. On account of the specified limitation generally placed on the amount of sulphate in cement, the presence of large amounts of sulphate in clinker reduces the amount of gypsum that can be interground with it. Since a large proportion (e.g. 40-70%) of the sulphate in clinker is not readily soluble (Stikker, 1958;[10] Anderlini & Vivian[1], unpublished data), cement made from it is deficient in readily soluble sulphate, its setting time is modified and its rate of strength development and shrinkage are adversely affected.

Potassium salts are generally more volatile than sodium salts. In some plants they have been extracted from precipitated kiln dust. This extraction process is not usually economic and can be improved only marginally by adding calcium chloride to raw meal, since the total amounts of alkalies in raw meal are low (approximately 1-2%) and increments in the amount of volatilized potash salt are limited. The demand for low alkali cement was first generated in some western areas of the United States where reactive siliceous components occurred in most aggregates. Subsequently the overall improvement noted in the quality of these cements has ensured a continuing demand for low alkali cement and has led to studies of the various procedures for reducing the alkali content of clinker.

Alkalies also affect clinker production in several different ways. In raw meal alkalies tend to reduce clinkering temperatures and generally increase the amount of liquid and the rate of clinkering. Simultaneously, however, alkali compounds penetrate a few centimetres into the kiln refractories and may react with the interstitial fosterite bond and with chromite to form alkali chromates. On account of differences between the coefficients of thermal expansion of basic brick and alkali compounds, large accumulations of alkali sulphates and chromates induce stresses which are additional to the high mechanical stresses resulting from kiln rotation, and accentuate the spalling tendency of brickwork.

Alkalies in Cement

The immediate solubility of alkalies constitutes one of their most noticeable properties. When cement is mixed with water a portion of the total alkalies, which depends partly on the sulphate content of clinker, dissolves rapidly. This quantity increases as the alkali-containing compounds hydrate. Soluble alkali salts in contact with hydrating clinker will inevitably be converted to alkali metal hydroxides and negative ions such as sulphate and carbonate will form less readily soluble calcium sulphate and calcium carbonate. The solution therefore rapidly approaches a transient ionic equilibrium and has a relatively large hydroxyl ion concentration which continues to increase with time. The presence of soluble alkali metal hydroxides depresses the solubility of calcium ion and modifies the rates of hydration of clinker compounds and of the early reactions that occur on clinker compound surfaces. These modifications influence the developing physical associations between large and small clinker particles and the physical state of newly-formed products. These changes in turn affect such characteristics as sedimentation, bleeding and stiffening, all of which may be used to describe the behaviour of cement paste.

Cement pastes have very high solid/water ratios and contain particles of different sizes. Consequently their properties are markedly affected by small differences in water contents. The performance of different cements may be quite variable and any chemical variation or measured physical change or property may be affected by a wide variety of factors which includes the conditions of clinker manufacture, the fineness of the cement and degree of aeration of clinker before grinding and of cement after grinding. Alkalies may interact with other factors to modify the chemical and physical changes which occur in paste. Steinour (1945)[9] has recorded experimental data showing that the bleeding rate and bleeding capacity of pastes decrease as their water-soluble alkali contents increase. In addition to clinker composition other factors including the rate of clinker cooling, grinding temperature, aeration, the addition of soluble salts and admixtures and test temperature are shows to affect the bleeding characteristics. Caution therefore should be exercised in drawing conclusions from data which represent rates of physical change in cement paste when the prior treatment and properties of the clinker and cement are not adequately described or controlled. While temperature typically modifies the rates of chemical reactions, the rate of physical change after mixing has ceased depends not only on imposed environmental conditions and on the quantities of clinker or clinker compound undergoing reaction and of newly-formed products, but also on the intrinsic properties of these latter products and their distribution in the paste. Consequently physical changes in pastes can be significantly affected by the occurrence of occlusion-type reactions that greatly restrict the rates but do not inhibit reactions, by changes in the physical nature of reaction products and by the conditions of temperature and water content imposed on the paste.

When cement and water are mixed together readily soluble compounds enter solution, solid particles, which are readily wetted and affected by various forces of attraction and repulsion, associate in arbitrarily sized masses, hydration and other chemical reactions commence and the observable physical characteristics of the paste such as sedimentation, bleeding and changes in workability become apparent. The paste very rapidly acquires a physical framework that will persist unless changed by the application of external forces, and all the future autogenous changes occur within this framework. As hydration proceeds minor chemical reactions and effects produced by their products are progressively obscured and obliterated by the more widespread chemical reactions, which yield large quantities of hydration products. Tricalcium silicate is therefore the clinker compound which largely determines the final performance characteristics of cement. Gel layers form rapidly on clinker particle surfaces and crystals grow into the surrounding solution. Continued hydration of clinker compounds disrupts the gel layers which rapidly re-form and, although crystals growing radially from adjacent clinker particles tend to interact, they do not become intergrown.

The solution in cement paste rapidly becomes supersaturated with respect to calcium and hydroxyl ions and approaches saturation with respect to sulphate ions. Since the amounts of alkalies in cement are relatively small, the sodium and potassium ion concentrations do not reach saturation. Lawrence (1966)[4] has discussed the composition of solutions in a number of cement pastes, and Fig. 1 records in a general way the changes which may occur in the soluble ion concentrations over the early hydration period (approximately 16-24 h).

As the hydration time increases the alkali and hydroxyl ion concentrations increase while sulphate and calcium ion concentrations decrease. It should be noted that cements generally contain more sulphate

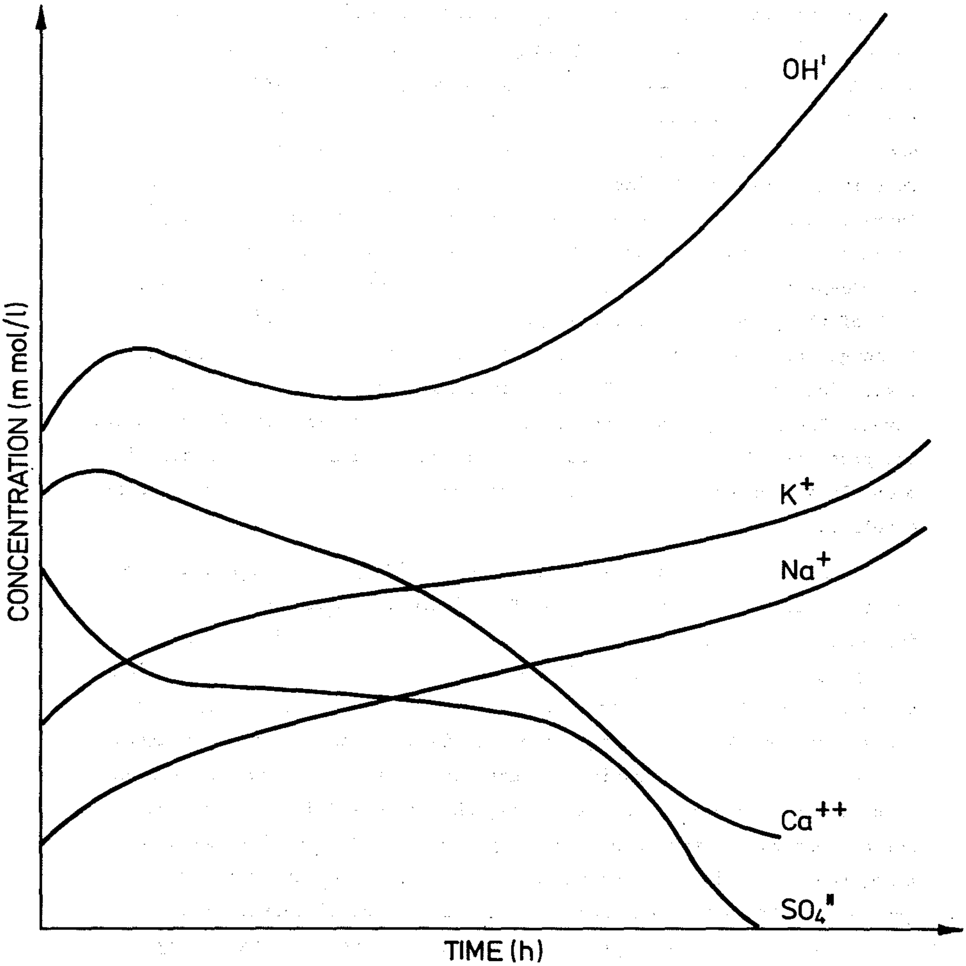

Fig. 1. Changes which occur in the composition of the solution phase in contact with hydrating cement.

ion than is needed to saturate the solution, especially at low water/cement ratios while excessively large amounts of both calcium and hydroxyl ions are continually being produced by the C_3S hydrolysis reactions. Although an increased water/cement ratio increases the amount of soluble sulphate, its concentration does not increase and in fact it decreases with time due to reaction with hydrated aluminate. There is also some evidence (Anderlini and Vivian, unpublished data)[1], which suggests that occlusion-type surface reactions especially in low water/cement ratio pastes, brtween C_3A hydrate and gypsum may prevent much of the potentially soluble gypsum from dissolving rapidly. Although the calcium ion concentration decreases with time and as the alkali ion concentrations increase, it remains above the saturation level. The hydroxyl ion concentration also remains correspondingly high. The presence of very small amounts of silicate and aluminate in solution probably indicates the adventitious occurrence of colloidal particles or micelles.

An increasing hydroxyl ion concentration promotes C_3A hydration and tends to retard the hydration of silicates. Simultaneously an increase in sulphate ion concentration reduces the solution pH, retards C_3A hydration and promotes silicate hydration. The amount of hydration which produces the early physical changes in paste is relatively minor. The effects of alkalies, either alone or in the presence of admixtures, on the properties of hydration products and on resultant phenomena such as strength development, permeability, shrinkage and durability, are largely unknown. Studies published by Lerch (1947)[5] described setting time, heat evolution and shrinkage of a number of cements which were ground to different finenesses and which contained different amount of C_3A, alkalies and added gypsum. In general cements containing large amounts of alkalies required large additions of gypsum to achieve adequate set retardation. It should be noted however that many of the factors which affect the behaviour and properties of a cement were not known or controlled in these experiments.

Although variations in the properties of different cements are relatively large, available evidence suggests that variations caused by alkalies are minimal compared with those caused by modifications in the major clinker compounds, by the degree of aeration, involving moisture and carbon dioxide, of clinker and cement, by fineness of grinding and by workability (water/cement ratio) differences. The fact that cement pastes and concretes made from both high and low alkali cements develop comparable characteristics suggests that alkalies do not cause major deleterious changes in the normal hydration and strength-gaining processes or in the nature of the hydration products.

Alkalies in Hardened Cement Paste and Concrete

Alkalies in hardened cement paste and concrete may influence reinforcement corrosion, the development of surface stains and efflorescence deposits, the incidence of surface scaling and "popouts", and the reaction with abnormal expansion of aggregates. The nature of the negative ion associated with positive alkali metal ion has a significant effect on the properties of the product and its action on the hardened mass. In addition the presence of potentially reactive materials and exposure to suitable environmental conditions or environmental cycling are necessary for some destructive actions to proceed.

Solutions of alkali metal hydroxides and calcium hydroxide, which have high pH's, passivate reinforcing steel surfaces and inhibit corrosion. Areas of the steel surface which are not completely coated with cement paste may undergo corrosion, especially if negative ions such as sulphate, chloride or carbonate are present to reduce the solution pH and to produce a conducting solution through which stray electric currents may discharge to earth. Moreover, too little cover over reinforcement or poorly compacted concrete allows the ingress of air, rapid carbonation of solutions, hydrated cement compounds and clinker particle surfaces and corrosion of reinforcement and disruption of concrete.

All types of concretes and concrete products as well as other porous solids can be affected by surface efflorescence deposits, staining and mould growth. Soluble alkali metal salts as well as calcium hydroxide and calcium salts may be deposited as white, crystalline, efflorescence deposits on concrete surfaces as the solution evaporates during periods of drying. These deposits, which vary from opaque coatings, which adhere tenaciously to the solid surface, to loose, fluffy masses, cause surface blotchiness, colour fading and general disfigurement of architectural surface finishes and features. On account of their insolubility in water, strongly adherent calcium carbonate coatings are difficult to remove. The loose coatings, which may sometimes be blown away, are usually readily soluble alkali salts which are re-dissolved by water, re-absorbed and later re-deposited when drying conditions recur. In addition the presence in aggregate of oxidizable compounds such as pyrite and marcasite, and organic matter which becomes soluble in alkali solution, promote the irregular staining of concrete surfaces with brown deposits. Apart from an occasional surface "pop-out" pyrite and marcasite are not usually present in sufficiently large amounts to cause undue physical damage to concrete. The staining deposits are also aesthetically undesirable rather than physically damaging.

When concrete is exposed to a sequence of drying and wetting cycles, in soluble salts tend to concentrate near the concrete surfaces. If present in sufficiently large amounts these salts may cause surface scaling, a phenomenon produced by shallow micro-pop-outs. When concrete is exposed to dry-wet cycling conditions, salts such as sodium sulphate are not only concentrated near the surface but also undergo a change from an anhydrous to a hydrated state. This change in the state of hydration of the salt is highly significant since unhydrated salts or salts which, although hydrated, are not readily crystallized, do not cause scaling. Removal of the surface layers of cement paste or mortar exposes the coarse aggregate which eventually becomes loosened, and produces a general roughening of the surface of the concrete. It should be noted that this scaling process is not confined to concrete; it occurs generally in permeable materials such as natural stone, sand-lime bricks and blocks and in certain earthenware ceramic products. Scaling causes more damage than efflorescence because it adversely affects the operating surfaces of structures and slowly reduces the section of structural units.

Alkalies in hardened concrete were shown to react slowly with siliceous aggregates which contain opal (Stanton 1940)[8] or which contain acid and intermediate volcanic glasses (Blanks and Meissner 1941)[2]. This reaction, which was discussed recently (Vivian, 1975)[12], produces quantities of an alkali hydroxide-silica complex which can absorb water and swell. The swelling complex exerts a disruptive force on the mortar surrounding the reacting aggregate particles. As cracks are formed and propagated through the concrete a significant overall expansion occurs. Since the concrete becomes extensively cracked its mechanical strength is markedly reduced and the space created by the cracks permits the ready entry of water or other salt solutions which may accelerate the disintegration of concrete exposed to adverse environmental conditions. It is impossible to control this reaction in large concrete masses which can undergo sufficient deterioration to cause the abandonment of the structure before it has completed its expected economic life. The testing of constructional materials before use and the prediction of the occurrence of this problem in concrete has now become widely accepted and practiced.

A somewhat similar but less widespread problem concerning the expansion of certain dolomitic aggregates in Canada and the United States has been reported by Swenson (1957)[11], Hadley (1961)[3] and others. Some dolomites have been shown to be capable of reacting with alkalies and causing concrete expansion. This reacting system possesses some unusual features which have not yet been fully explained and the precise source of the disruptive forces has not been clearly demonstrated. Nevertheless this reaction suggests that the presence of relatively large amounts of alkalies in cement and their reaction with a susceptible dolomitic aggregate can cause large concrete expansions. To obliviate damage from this source tests have been devised to permit the prediction of aggregate behaviour in concrete.

Economic Effects of Alkalies in Cement and Concrete

For much of the concrete that is produced the alkali contents (generally <1%w/w of cement and consequently <0.2% w/w of concrete) are so small that they have no significant adverse effects on desired properties. Moreover, unless other significant factors are present, in general constructional concrete, alkalies do not cause any adverse material modifications. Alkalies do not produce any significant changes in concrete that is kept completely and continuously wet is also relatively unaffected by alkalies. Exposed concrete, which is subjected to intermittent wetting and drying or subjected to water pressures on one face, may develop the typical wet-dry cycling effects which, if other essential factors are present, can include general deterioration, surface staining, efflorescence and scaling. The fact stands out quite clearly that, in evaluating the economic impact of any potential problem in concrete, environmental exposure conditions must be considered along with various material and structural factors.

Consideration of the economic effects of alkalies involves the cost of prior investigations of sites and materials. It also involves the maintenance of operation of the structure and the cost of repairing damage such as staining caused by efflorescence and mould growth on architectural concrete finishes and surface scaling. Greater costs can be caused by the need to reconstruct a defective structure before its estimated economic life has elapsed. Since cement is manufactured and is usually the major source of alkalies in concrete, economic considerations tend to become involved with procedures for removing alkalies from clinker. Alkalies derived from ground-water or general working operations may sometimes cause problems which can only be prevented by good construction practices and surface protection.

In certain localities where all available aggregates are considered to be potentially reactive, a maximum alkali content has been specified for cement. Stanton (1949)[8] initially proposed as a maximum limit 0.5% total alkalies expressed as $\%Na_2O + 0.658\%K_2O$, and subsequently increased this maximum to 0.6%. This latter figure has been generally adopted as the limiting quantity which separates high from low alkali cements. It is quite possible that this arbitrary limit may still be too high because over long periods of time alkalies may concentrate in a relatively few areas and cause such damaging effects as surface efflorescence, scaling and aggregate expansion.

Since the cost of removing alkalies from clinker is high, it is essential where possible to choose raw materials that have low alkali contents. If such materials are not available, removal of a portion of the alkalies during clinker manufacture is more economic than their complete removal. The alkali contents of many low alkali cements are therefor just below the maximum limit. It will be seen that changes which are intended to reduce alkali contents may induce additional problems which reduce production rates and increase maintenance costs. Although volatilization of an increased amount of alkalies from raw meal by high burning temperatures may assist in producing a high quality clinker, it also increases fuel and kiln lining costs and may reduce output. Additions of compounds such as calcium chloride to raw meals or to fuel to increase the amount of volatilized alkalies are generally ineffective, increase costs and may induce additional corrosion and clogging problems in exhaust systems. Although dumping precipitated kiln dust in contrast the returning dust to the kiln, assists in reducing the alkali content of clinker, this practice wastes valuable material, reduces kiln output and therefore directly increases production costs. This practice also increases handling problems and accentuates the need for either storage or dumping space so that a pollution problem is not created.

Abrasion and corrosion of metal in plant units may be severe. The presence of calcium chloride dusts and moisture in flues, stacks and hoppers where temperatures fall sufficiently low for moisture to condense may accelerate metal corrosion. On the other hand the rate of steel losses from grinding media and liner plates in ball mills is up to 10 times greater in wet than in dry grinding mills. This difference is due to corrosion which can be significantly reduced by increasing the pH of the slurry (Anderlini and Vivian, 1961)[1]. Although such an increase in pH would increase the alkali content of clinker slightly and modify the flow characteristics of the slurry, it could be an econimically viable addition in some plants.

The production of blended fly ash-portland cement mixtures can also affect alkali contents. If the alkali content of the fly ash is low, the overall alkali content of the blended cement can be effectively reduced. This reduction in alkali content has been regarded as one of the advantages of blending a pozzolan with portland cement to reduce the extent of alkali-aggregate reaction. However some fly ashes from coal-fired boilers contain large amounts (>5%) of alkalies and consequently in blended cements could significantly increase the alkali content of concrete.

The permeability of concrete and concrete products affects the incidence of efflorescence and scaling. Reduced permeability improves the general quality and performance of concrete significantly. It has long been recognised that the processes of glazing ceramic ware and of polishing natural stone seal the product surfaces and either eliminate or significantly reduce the movement of solutions under cycling environmental conditions. A reduced permeability in low priced concrete and concrete products which can be achieved without the use of costly material or production treatments would reduce the movement of solutions. Consequently any procedure that enables high density cement pastes to be produced without the need for large compacting pressures could be a suitable alternative to reducing the alkali content of cement. A reduction in paste permeability may be achieved by grinding cement more effectively and modifying its mean particle shape so that adequate workability is developed at a reduced water content.

Concluding remarks

1. Alkalies are present in varying amounts in all cements and concretes. They do not affect the performance of cement adversely

and compared with other major components, their effects on many of the properties of concrete are small.

2 Alkalies may cause some surface blemishes in concrete such as:-

(a) staining,
(b) efflorescence, and
(c) scaling.

3 Alkalies may cause more complex and damaging effects in concrete such as:

(a) reaction with siliceous aggregates, and
(b) reaction with dolomitic aggregates.

4 Alkalies produce strongly alkaline solutions which have the beneficial effect of inhibiting reinforcement corrosion and minimizing steel media and liner plate corrosion in wet grinding mills.

5 Wet-dry cycling exposure conditions are necessary to produce severe efflorescence and scaling problems. Exposure to continuously wet or dry conditions does not cause marked efflorescence or scaling.

6 The presence of some alkali in cement and concrete must be accepted since it is neither technically nor economically feasible to remove alkalies completely. Some reduction in the amount of alkalies in cement can be achieved by:

(a) Choice of low-alkali raw materials.
(b) Increased volatilization of alkalies by high burning temperatures. This procedure also increases fuel costs and may reduce kiln lining life and kiln output.
(c) Additions such as calcium chloride to raw meal to increase the volatilization of alkalies. This may also increase corrosion and dust collection problems.
(d) Non-recirculation of precipitated kiln dust which may be dumped or used as a lime top-dressing for pastures.

7 Improvement in the performance of concrete may be achieved by:

(a) The use of low alkali (<0.6%) cements.
(b) The use of blends containing suitable amounts of pozzolans such as burnt clays, volcanic ashes or fly ashes.
(c) The substitution of non-reactive aggregates for known reactive aggregates

(d) The use of surface treatments or barriers to prevent alkali-containing ground water from being absorbed by concrete.

8 Aggregates should be tested prior to use and those containing deleterious components discarded. Standard tests are available for this purpose. It should be noted however that these tests alone are not suitable for assessing the probable behaviour of the material under operating exposure conditions.

9 An improvement in concrete performance could be accomplished by reducing the permeability of cement paste. By modifying the shape of cement particles and reducing the water/cement ratio, the rate of movement of solutions in concrete could be restricted sufficiently to minimise the staining, efflorescence and scaling problems and other desirable physical properties of cement could be improved. Good constructional practices would still be essential to ensure complete compaction and tight joints and to eliminate undue cracking.

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CONTRIBUTIONS TO DISCUSSION

Mr. B. Mather

Firstly, I join Miss Moore in expressing regret that Mr. Vivian is not present. Second, I applaud the emphasis given in paragraph 1 of part 5 of the paper on environmental effects especially the statment "Alkalies do not produce any significant changes in concrete that is dried out and is then kept continuously dry". Third: I inquire whether there is documentation that alkalies in cement cause or encourage "mould growth" as noted in the second paragraph of part 5. Finally with regard to the point about high-alkali fly ashes as noted in the next to the last paragraph, at our laboratory we evaluated fly ashes of various alkali contents for effectiveness in reducing expansion of pyrex glass - high alkali cement mortar bars. High-alkali fly ashes were less effective than low-alkali but when used in appropriate (larger) amounts were equally effective; these higher amounts are reasonable and economical especially in mass concrete.

Mrs. K. Mather

I would question Vivian's point: "Alkalies do not produce any significant changes in concrete that is dried out and kept dry"; How does this compare with the Hadley explanation of reaction with low alkali cement in the semi-arid climate of Kansas and Nebraska where drying the concrete concentrates the alkali from low alkali cement and permits reaction to occur. Answer to question by B. Mather is that the concrete in Kansas was occasionally subject to being rained on; thus a different situation than Vivian envisioned.

Ms. A.E. Moore

In Section 2, paragraph 3, H.E. Vivian suggests that high sulphur fuels promote retention of alkalies and then that this may result in a large proportion of clinker sulphate which is not readily soluble. Surely alkali sulphate is highly soluble, and indeed the first line of Section 3 says this? Pollit and Brown (Tokyo Symposium) show that it is very unusual to have less than 70% of clinker sulphate readily soluble.

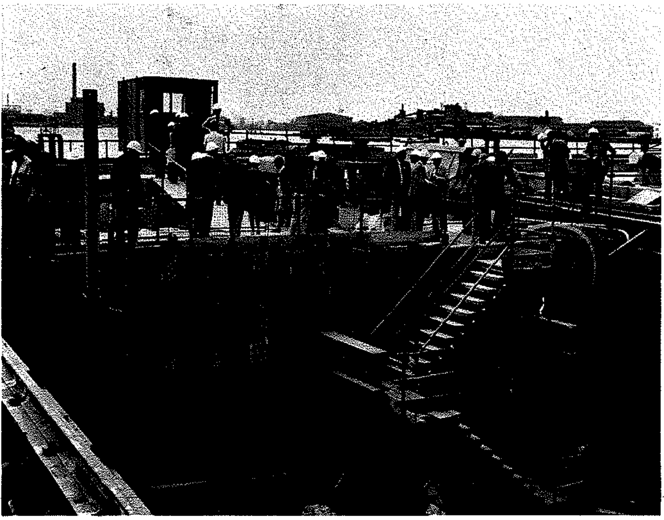
Mr. P.J. Jackson

1) On Page 11 the claim is made that recirculation of reclaimed precipitation dust generally changes the raw meal composition adversely. This contribution has been involved with this reaction for a decade now, and provided it is correctly carried out has found no such adverse effects.

2) On Page 12 it is noted that quality is said to improve with low alkali cements. This contribution is not clear what is meant by this. Certainly as far as strength and many other properties are concerned high alkali cements can be as good as or better than some low alkali cements. This matter is dependent on so many other considerations that a generalisation such as this is not warranted.

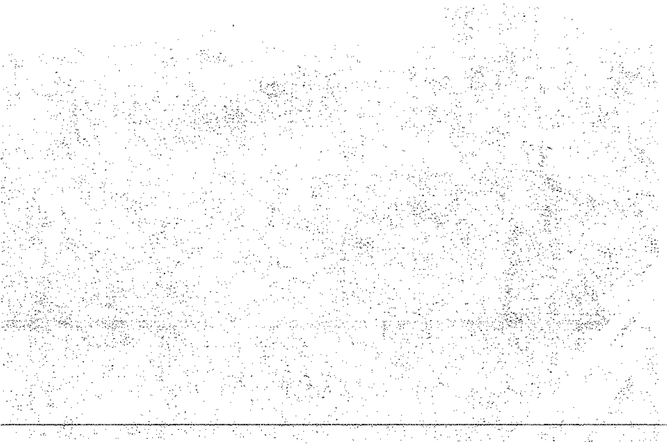
Mr. J. Figg

A possible explanation concerning Mr. Mather's query is that mould growth will be inhibited in high alkali environments and this may be the effect referred to in H.E. Vivian's paper.



The Thames Barrage Site

2. ALKALIES IN CEMENT AND CEMENT MANUFACTURE



ALKALI COMPOUND FORMATION OF COMMERCIAL PORTLAND CEMENT CLINKERS

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ABSTRACT

The effect of kiln atmosphere in the burning zone on the formation of alkali compounds was studied. It was concluded that the double salt $K_3N\overline{\underline{S}}_4$ was produced under reduced kiln conditions while C_2KS_3 tended to be formed under oxidizing conditions.

The data I wish to present to this conference was based upon x-ray diffraction studies of alkali sulfate compound formations of some commercial clinkers. The effect of reduced clinkers have been the subject of various investigations in the past (1,2), and also much has been published on the alkali sulfate compounds (3,4) in cement clinkers. This study seems to indicate that the atmosphere in the burning zone can have as much influence on the alkali sulfate compound formation as does the chemical composition. These conclusions are tentative and could be modified as additional information is obtained from the ionic concentration of the liquid phase studies currently underway. The effect of these alkali compounds on early hydration is also being investigated.

This study was prompted by two relatively recent events which occurred in the cement industry of the United States.

1. The sudden fuel shortage made it necessary for plants which had previously burned natural gas and/or oil to switch to less expensive coal containing higher sulfur.

2. Increasing field complaints because of variable water demand, variable setting times, and incompatability with some admixtures were registered.

I will report on only six of over one hundred commercial clinker composites which were analyzed. The clinkers discussed in this paper were produced in commercial kilns to which various amounts of dust were returned. The criteria for selection were based on two factors:

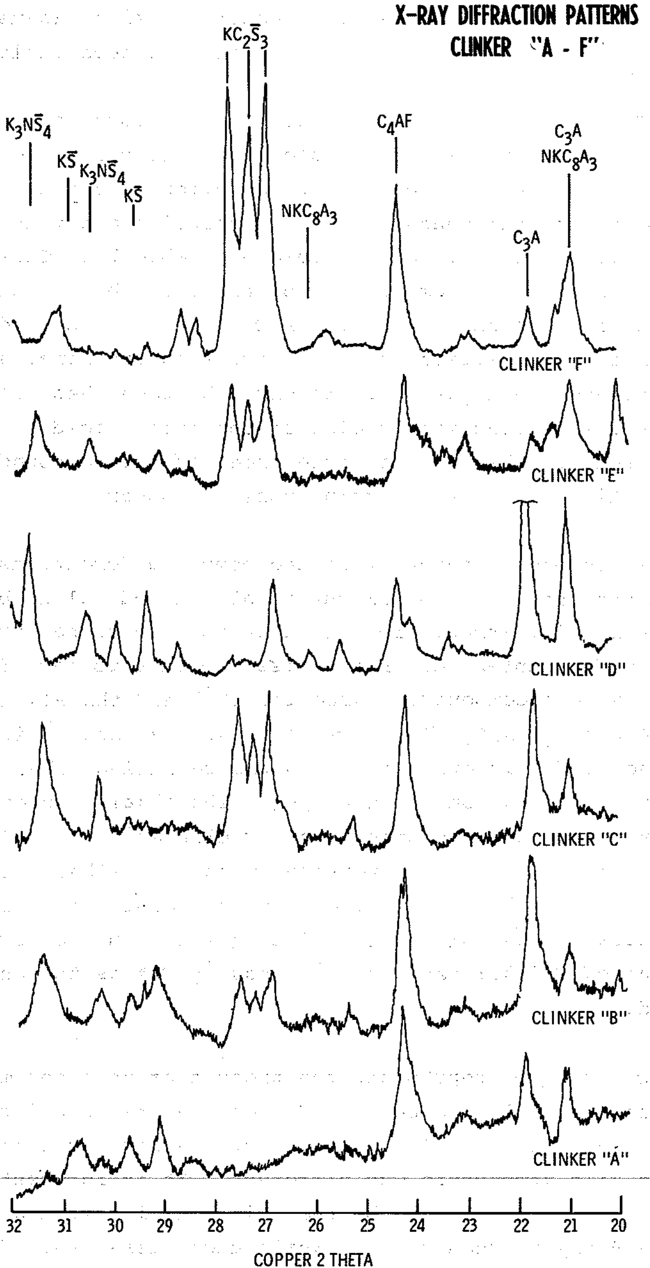
1. The amount of alkalies and sulfates in the clinker.
2. The estimated oxygen deficiency in the burning zone during the production of these clinkers.

The chemical analyses of these clinkers (Table 1) exhibit a general range of alkalies and sulfur which could be expected during various production periods. Naturally, when the clinker alkali and sulfur reach the upper control limits, adjustments to kiln parameters are made to lower them to acceptable limits.

The primary method of alkali sulfate compound determination was by x-ray diffraction studies of the maleic acid residues(5). Figure 1 shows the XRD scans of these clinkers and the Cu 2-theta location of the compounds. Atomic absorption analysis of the maleic acid filtrate is also tabulated (Table 2). This analysis relates the chemical composition of the alite-belite phases plus the free lime content. Except for Clinker "D" one finds that the chemical composition of the silicate phases remains rather constant, and the greatest differences between these clinkers are found in the diffraction studies of the maleic acid residue. Table 3 relates the salient differences of the compound products and an estimation of the burning zone atmosphere.

It becomes apparent that the compound formations are contingent upon not only the amount of alkali and sulfur but also upon the burning atmosphere. Clinker "A", which has the lowest alkali sulfur content of this series, appears to have formed only two alkali compounds: arcanite ($K\bar{S}$) and the alkali substituted C_3A $[(N,K)C_8A_3]$. One could assume that $K\bar{S}$ is formed until the sulfur is exhausted then the remaining alkali is consumed in the formation of $(N,K)C_8A_3$. The alkali preference for sulfur appears to be substantiated by Clinker "B" and "C" which differ from "A" only by increasing amounts of alkali and sulfur. In the "B" and "C" clinkers there is the formation of calcium langbeinite ($KC_2\bar{S}_3$) and aphthitalite ($K_3N\bar{S}_4$) in preference to $(N,K)C_8A_3$ of Clinker "A"; thereby leaving C_3A as the only alumina compound.

Clinker "D" represents the product of an experimental burn which inadvertently was conducted under severe reducing conditions, while Clinker "E" was collected a few hours earlier. Only the kiln atmosphere was different. It is interesting to note that $K_3N\bar{S}_4$ appears to be the only alkali compound present in the severly reduced clinker while under less reduced conditions the clinker gave strong diffraction patterns for both $KC_2\bar{S}_3$ and $(N,K)C_8A_3$. This would seem to indicate that $K_3N\bar{S}_4$



X-RAY DIFFRACTION PATTERNS
CLINKER "A - F"

FIGURE 1

is a preferential compound when produced in a reduced kiln atmosphere.

Clinker "F" would again seem to support the hypothesis that kiln atmosphere can dictate minor compound formation. This clinker was the product of another experimental burn in which every effort was made to maintain an oxidizing flame. The major alkali compounds of this clinker appear to be the same as Clinker "E": $(N,K)C_8A_3$ and $KC_2\bar{S}_3$. As mentioned earlier, these samples were selected from many that have been analyzed. These particular clinkers were selected to illustrate a relatively high degree of purity of the alkali sulfur compounds. We have diffraction patterns on which we have identified the presence of $K_{.67}N_{1.33}\bar{S}_2$*. We have also observed peak shifts for the above compound which indicate that a considerable range of the solid solution series of $K_xN_y\bar{S}_z$ (where $x + y = z$) compounds may be possible constituents of portland cement clinker.

Evaluations of the maleic acid filtrate analysis of these clinkers (Table 3) indicate that only minor portions of the alkalies and sulfur are found in the silicate phases. This gives additional support to the x-ray diffraction studies which place the majority of these elements in alkali sulfate and/or alkali aluminate compounds.

In summary these data would seem to suggest:

1. The preferential compound formation for alkalies in cement clinker is in some combination with the sulfur. When the sulfur has been depleted the alkalies appear to form $(N,K)C_8A_3$ as the next most preferential compound.

2. The burning zone atmosphere seems to dictate which alkali sulfate compound is formed. $KC_2\bar{S}_3$ tends to be produced in an oxidized flame while the excess

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*JCPDS Pattern 20-926

alkalies form $(N,K)C_8A_3$. $K_3N\bar{S}_4$ appears to be formed during periods of reduced burning conditions and any excess alkalies going into the silicate phases.

TABLE 1

Clinkers Chemical Analysis (%)

CLINKER	A	B	C	D	E	F
SiO_2	21.60	21.20	21.30	21.34	21.25	21.80
Al_2O_3	5.95	5.80	5.85	6.21	6.05	4.40
Total Fe as Fe_2O_3	2.60	2.70	2.65	2.38	2.51	3.00
FeO	0.05	0.15	0.05	0.93	0.15	0.01
CaO	65.80	64.50	63.30	63.52	63.42	61.92
MgO	3.00	2.90	2.85	2.43	2.46	4.44
P_2O_5	0.10	0.01	0.01	0.28	0.13	0.11
TiO_2	0.25	0.20	0.25	0.26	0.26	0.20
Na_2O	0.25	0.25	0.25	0.44	0.48	0.23
K_2O	0.55	0.95	1.10	0.82	1.41	1.11
SO_3	0.40	1.80	2.50	1.56	1.01	2.90
Sulfide Sulfur as SO_3	0	0	0	0.62	0.05	0
LOI	0.15	0.20	0.30	0.55 wt.gain	0.09	0.41
Free CaO	0.40	0.40	0.80	1.21	0.80	0.30
Bogue Potential Compounds						
C_3S	58.88	53.50	45.59	46.83	49.57	44.28
C_2S	17.51	20.42	26.67	25.85	23.53	29.10
C_3A	11.37	10.80	11.02	12.43	11.79	6.58
C_4AF	7.91	8.22	8.06	7.24	7.64	9.13

TABLE 2

Maleic Acid Filtrate Analysis (%)

Clinker	A	B	C	D	E	F
SiO_2	20.77	20.55	20.54	21.12	22.09	21.74
Al_2O_3	0.94	1.30	1.00	0.86	0.80	1.45
Fe_2O_3	0.52	0.62	0.72	0.53	0.58	0.59
CaO	55.05	53.93	52.78	53.28	54.42	53.95
MgO	1.29	1.09	0.94	0.82	0.96	1.17
SO_3	0.05	0.06	0.07	0.13	0.11	0.15
Na_2O	0.09	0.10	0.10	0.14	0.15	0.11
K_2O	0.21	0.26	0.20	0.33	0.21	0.16

TABLE 3

Compound Intensities vs Kiln Atmosphere

Clinker	A	B	C	D	E	F
			Alkali Sulfur Analysis			
SO_3	0.40	1.80	2.50	0.94	0.96	2.98
K_2O	0.55	0.95	1.10	0.82	1.41	1.11
Na_2O	0.25	0.25	0.25	0.44	0.48	0.23
			Kiln Atmosphere			
	Slight Reduced	Reduced	Reduced	Extreme Reduced	Slight Reduced	Oxidixed
$KC_2\bar{S}_3$	O	W	S	W	S	VS
$K_3N\bar{S}_4$	O	M	S	VS	W	O
$K\bar{S}$	W	O	W	W	W	W
$(N,K)C_8A_3$	M	W	W	O	S	VS
C_3A	M	S	S	VS	W	W

O = None Detected
W = Weak Intensity
M = Medium Intensity
S = Strong Intensity
VS = Very StrongIntensity

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SHORT REPORT ON OPERATING A MODERN CEMENT WORKS

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ABSTRACT

During 1971-1974 a complete new plant was built at our old De Hoek Works. Features of the new plant include:
A sophisticated system of pre-blending raw materials from the quarry which permits the feeding of a thoroughly blended material to the next stage of production. Samples of the material are taken by an automatic sampler and are analysed by an X-ray fluorescence spectrometer, with the results being fed directly into a process control computer. The chemical analysis is also used for the next stage of the process for automatically controlling the rates of feed to the raw mill. The X-ray fluorescence spectrometer accurately determines the calcium, silica, iron, sulphur, magnesium, alumina and potassium content of the materials concerned within two minutes.
The kiln incorporates a 4-stage preheater cyclone system and the whole operation is controlled by extensive automation and instrumentation operating from a centralised control room. On the whole, the plant has performed well, except for a series of chokes in the preheating system. The frequency of these has been considerably diminished by various physical modifications and some alterations to operating procedures.

The Company and the Works

The Cape Portland Cement Company was incorporated in 1921 with an original share capital of R700 000. It took over the assets of the Hermon & Picquetberg Lime Company and established its first factory at De Hoek about six kilometers from Piketberg.

The initial manufacturing capacity was 54 000 tonnes of cement per year and this was increased through the following thirty years to reach 270 000 tonnes per year. The next extensions were at Riebeek West where a kiln was started in 1959 and a further extension in 1968 brought the production capacity of the Company to roughly 820 000 tonnes of cement per annum.

When the demand for cement further increased, it was decided to replace the old plant at De Hoek with a new, modern plant. Construction of this plant started in late 1971 with the kiln being commissioned in June, 1974. The final cost of the new plant was roughly fifteen and a half million Rand and it is capable of producing approximately 500 000 tonnes of cement per year.

The Raw Materials

Limestone

A hard, blue-grey, secondary limestone, extracted by open-cast mining methods from a quarry adjacent to the Works. The material is drilled and blasted and then transported to the primary jaw crusher situated within the quarry. The crushed material (-150 mm) is raised by a conveyor belt to the secondary crusher station sited at the surface, next to the quarry. This station houses twin units, each consisting of a triple-deck vibrating screen and a Hazemag impact breaker. The oversize material is crushed (95%-25 mm) whilst the smaller sized fractions coming from the quarry can either be diverted to the waste dump or combined with the crusher product, which is conveyed to a stockpile. There are two stockpiles of low/medium grade "run-of-quarry" limestone and one high-grade pile.

TABLE 1

Typical Analyses of Limestone Samples ex Crushers

Constituents/ Ratios	Low/Medium grade		High grade	
	%	%	%	%
SiO_2	13,5	11,5	9,1	6,5
Al_2O_3	3,0	2,5	2,1	2,2
Fe_2O_3	1,0	0,5	0,6	0,9
Ca O	46,7	48,9	50,1	51,0
SO_3	0,3	0,2	0,4	0,4
K_2O	0,7	0,5	0,5	0,4
MgO	1,5	1,3	1,2	0,9
Na_2O	0,4	0,2	0,3	0,3
Cl	0,007	0,004	n.a.	n.a.
L.S.F.	111,5	135,3	176,2	236,7
Silica Ratio	3,4	3,5	3,5	2,1
A/F	3,0	3,1	3,6	2,4

TABLE 2

Variation of K_2O and SO_3 content in Limestone Samples

Sample No.	L S F %	K_2O %	SO_3 %
1	100,6	0,78	0,71
2	121,2	0,64	0,57
3	133,1	0,62	0,81
4	136,2	0,65	0,71
5	146,2	0,58	0,73
6	150,2	0,81	0,63
7	161,7	0,69	0,81
8	167,5	0,46	0,63
9	166,9	0,44	0,86
10	178,9	0,41	0,83
11	208,8	0,25	0,51
12	220,2	0,25	0,51
13	262,8	0,16	0,45
14	283,0	0,26	0,52
15	286,4	0,08	0,53

Shale

Most of the overburden on top of the limestone, and the material surrounding it, consists of a soft yellow shale. Prior to installing the new plant at the Works the raw mix used to consist solely of limestone and shale. Much of the limestone deposit consists of a mixture of a slightly harder grey shale (with a composition similar to that of the yellow shale) and the much harder limestone. When there is an excessive amount of shale mixed with the limestone it is screened out, as described above, to upgrade the quality.

Yellow shale is extracted and fed through the system as and when required, and stored in a separate stockpile.

TABLE 3

Typical Analyses of Shale Samples ex Crushers

Constituents	%	%	%	%
SiO_2	65,5	71,5	60,2	57,0
Al_2O_3	12,8	13,4	16,4	17,1
Fe_2O_3	8,7	9,2	7,5	8,0
CaO	-	-	2,8	4,2
SO_3	-	-	0,1	0,4
K_2O	2,8	2,8	3,3	2,8
MgO	1,1	1,0	1,6	1,4
Na_2O	n.a.	n.a.	0,4	0,7
Cl	n.a.	n.a.	0,1	0,1

Sand and Iron Ore

About 2% of river sand and 1,2% of iron ore (haematite) are added to the raw mix (on average) in order to keep the silica and A/F ratios as constant as possible.

TABLE 4

Typical Analyses of Sand and Iron Ore Samples

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	K_2O	MgO	Na_2O	Cl
	%	%	%	%	%	%	%	%	%
Sand	97,7	1,2	0,8	0,03	-	0,3	0,1	0,1	0,04
Iron Ore	17,3	3,9	66,2	1,2	0,2	0,5	0,7	0,3	tr.

THE RAW MIX CONTROL

Equipment

X-ray Spectrometer:

Make: Siemens

Type: Multichannel MRS-2T

X-ray tube: Ag Cr 61 with chrome anode

Elements: Fe Mg S Ca K Al Si

Crystal: LiF100 AdP PET Quartz PET PET PET

Counting time: 2 min.

Tube: KV/MA 50/44

Press: Hertzog Automatic Press

Communication between X-ray spectrometer and computer is established by means of the following signals: 32 digital inputs, 4 digital interrupts and 14 digital outputs from S/7.

Computer:

Make: IBM S/7 Model A16

Storage: 16 K words, each consisting of 16 bits

Typewriters: 1 - 5028 operator station
2 - 1053 printers

Disks: 1 Fixed
4 Removeable

Power failure interrupt

Automatic restart

Interval times

Analog inputs 96

Digital inputs 128 (32 Process interrupt)

Digital outputs 48

Samplers:

1. SALA sampler

   Situated between the secondary crushers and the preblending stacker, this device automatically samples (at pre-set intervals) all material being conveyed to the various stockpiles; it reduces the sampled material to a coarse powder and splits and mixes it. When the sample is collected a button is pressed to indicate to the computer that this has been done, and the computer then "reads" the belt weigher in order to determine the quantity (in tonnes) of material which the sample represents.

2. FLS Raw mix sampler

   Situated after the raw mill.

Plant:

1. Weserhütte Preblending Stacker and Reclaimers:

   The stacker lays down the piles of crushed limestone in a series of 400 longitudinal layers, arranged in the "windrow" fashion (NOT chevron pattern). There are two "run-of-quarry" limestone stockpiles, one high-grade limestone pile, and one shale stockpile. The reclaimers are fitted with swivelling bucket-wheels which cut across the entire 400 layers (built-up over several days) each 5 minutes. The theoretical blending effect is 20 : 1 (i.e. square root of 400), and, as far as can be ascertained, this is borne out in practice.

2. Two storage silos:

   One for river sand and one for iron ore.

3. Schenck weighing equipment:

   Belt weighers to record rate and weight of material stockpiled, and control speed of stacker, and reclaiming rates.

   Four weigh-feeders, controlled by the computer, to proportion and control the feed to the raw mill.

4. F.L. Smidth Raw Mill:

   Tirax-unidan mill, rated at 110 tonnes per hour for a product with 10% residue on the 170 mesh screen.

5. Two Claudius Peters Homogenising Silos:

   Each of 6000 tonnes capacity, and fitted with a "misch kammer". Guaranteed to have a blending effect of 5 : 1.

Control:

1. Raw Materials Preblending:

   The raw materials are fed to the prehomogonising store via a belt weigher and an automatic sampler. The material is deposited on one of four piles. An account is kept by the computer of the contents, in tonnes, of wet materials in each pile. During the filling up of a pile, the average chemical analysis is calculated

   The basis for these calculations is:

   Samples taken out by the automatic sampler, as well as analog and digital signals from the prehomogonising store and the feeders of the raw mill.

2. Raw milling:

The quality of the kiln feed is controlled by blending four, three or two raw materials. The chemical requirements as regards the kiln feed are determined by setpoints for:

(1) LSF
(2) SR
(3) A/F

The quality of the kiln feed is controlled on the basis of average raw mix samples taken after the Raw Mill.

The chemical requirements as regarding the raw mix are determined as follows: After passing the Claudius Peters homogenising silos, the raw mix should fulfill the required setpoints as far as possible. The automatic sampler of the raw mill is emptied about once every hour. The analysis of this average sample, and the corresponding consumption in tonnes of each of the four raw materials, is used for up-dating the limestone analysis. The knowledge of the raw materials analysis and the deviations accumulated are used in the calculation of the proportioning of the raw materials to be fed to the raw mill in the next hour.

3. X-ray Analysis and Control:

A raw mix sample is taken every hour mixed and analysed.

The analytical procedure used is:

Grind 40 gram Raw Mix + 0,5 gram Boric Acid for 4 minutes in a Bleuler Ring Mill. 29 Grams of ground material + 1 gram wax is then mixed for 2 minutes. A special communications code is then dialed indicating to the computer the type of analysis, production line, type sample and sample no. The sample is then fed to the press, the spectrometer started, and 4½ minutes later the results are typed out on the one 1053 printer. New % setpoints are also automatically calculated for the 4 feeders and printed on the other 1053 printer. The feeders are set to the new percentages by the computer, and a new updated limestone analysis is calculated.

The X-ray is serviced daily by laboratory assistants and standard samples (tablets) are analysed. If these analyses are out of limits (0.5 LSF, 0,1 SR and 0,1 A/F) the X-ray is recalibrated. Once a shift a quality control sample is analysed - including sample preparation. These analyses are used to check the accuracy of the spectrometer and the sample preparation. A number of safety precautions are incorporated in the computer programs to prevent the analysis of the wrong material as raw mix. Measurement of relative half-width is done every month as further check on the spectrometer.

The X-ray is at present used to analyse raw mix, kiln feed, limestone, filter dust, clinker and cement (for gypsum control).

TABLE 5

Typical analyses of limestone and shale ex stockpiles, raw meal ex mill, and raw mix as fed to kiln (i.e. after silos).

Constituents	Limestone %	Shale %	Raw meal %	Kiln feed %
SiO_2	9,9	64,5	13,8	13,7
Al_2O_3	2,4	12,9	2,9	2,9
Fe_2O_3	0,9	8,3	2,3	2,2
CaO	46,5	0,01	42,9	43,1
SO_3	0,4	-	0,7	0,8
K_2O	0,6	2,9	0,8	0,8
MgO	1,3	1,1	0,9	1,0
Na_2O	n.a.	n.a.	n.a.	0,1
Water-soluble Cl	n.a.	n.a.	n.a.	0,01

TABLE 6

Weekly Clinker Analyses for Five weeks

Week ended :	20.6.76	27.6.76	4.7.76	11.7.76	18.7.76
SiO_2	21,2	21,2	21,2	21,1	21,2
Al_2O_3	5,6	5,6	5,5	5,7	5,7
Fe_2O_3	3,7	3,6	3,6	3,6	3,7
CaO	65,3	65,4	65,4	65,4	65,3
SO_3	0,9	0,8	0,9	0,8	0,8
K_2O	1,0	1,0	1,0	1,0	1,0
MgO	1,7	1,8	1,8	1,8	1,7
Na_2O	0,2	0,2	0,2	0,2	0,3
Loss on Ign.	0,3	0,3	0,3	0,3	0,3
L.S.F.	95,5	95,7	95,9	96,0	95,3
S.R.	2,28	2,30	2,33	2,27	2,26
A/F	1,51	1,56	1,53	1,58	1,54

THE KILN

An F.L. Smidth (Denmark) kiln, with a 4-stage preheater consisting of twin first-stage cyclones and single second-,third- and fourth-stage cyclones. The kiln is 66 m long and has an internal diameter (before lining) of 4,35 m. It is fitted with an F.L.S. conditioning tower and electrofilter. Raw meal feed-rate is controlled by means of a Schenck solids-flowmeter and the kiln is coal fired, and consumes approximately 3,43 MJ/kg clinker (820 k.cals/kg.). Operation commenced on 20 June 1974.

Guaranteed output rate of clinker is 1150 metric tonnes per day, but the kiln operates comfortably anywhere in the range 1050 to 1350 tonnes per day. It has been operated as low as 950 and as high as 1390 (possibly even higher) tonnes per day, but at these extremes constant supervision is necessary.

It was predicted by F.L.S., from the alkali/sulphate ratios of our materials, that we could expect a "soft" build-up in the riser pipe between the kiln and the 4th-stage cyclone, and that this material would harden if it was not removed on a regular basis. This has been the case, and the material is removed twice a shift by poking through holes provided. If this is not done the pressure drop in this area builds up visibly on the chart. In two years of operation it has not been necessary to stop the kiln for a major build-up in this area.

Build-ups of material (also relatively soft) have occurred at various points in the cyclone pre-heater system, and after 22 weeks operation (twice) these have apparently started breaking up under their own weight, and the lumps falling down have caused chokes in ducts where there are restrictions, in some cases resulting in cyclones filling up with hot material. This has necessitated stopping the kiln for a day until the cyclone was cleared. Various modifications have been made to overcome this problem, as described below:

Physical Modifications:

March 1975 (during first major kiln shut-down)

1. Thermocouple removed from feed pipe below No. 4 cyclone into kiln and resited in the cyclone itself. (This caused several chokes by trapping lumps which would otherwise have passed through into the kiln).

2. The flexible joint in the above pipe was moved to a different position, and poke holes were provided.
3. Additional poke holes were provided throughout the system.
4. An inspection door was provided in the top of the 4th cyclone so that a ledge, where material settles, can be cleaned when necessary.

November 1975

5. All flexible joints were lagged (to prevent "condensation" of hot material).

Feb./March 1976 (during second major shut-down)

6. Alteration to inlet of No. 4 cyclone - to change its shape to the approximate "natural" shape caused by build-ups in this area - as recommended by F.L.S.

May 1976

7. Air jets provided at the "splash-plate" at the entrance of the feed pipe from No.3 cyclone. (This splash plate had become distorted and was removed on 22 Jan. 1976 as it was obviously causing chokes. During March '76 it was replaced with a thicker, stronger plate, but there was still a tendency to choke on start-up. Operating the airjets for about an hour after each start-up has prevented further chokes in this area).

Operational Changes:

1. Reduce feed-rate to kiln before any planned stops of the kiln. Because of the long "feed-line", if this is not done, on restarting the kiln it is initially "flooded", and then "starved" - during which period material (consisting mostly of dust return) gets over-heated and tends to form lumps.
2. STOP the kiln immediately at the first indications (given by instruments) of a possible choke. The first few times inspections were made (without stopping) and/or instruments were checked, by which time a minor choke had become a major choke.
3. Regular, careful maintenance of the conditioning tower. Faults in this system result in it choking, which reduces the total amount of material going to the kiln and this results in overheating in the preheater.
4. The dust return system is emptied during stops. Otherwise "uncontrolled" amounts of material are fed to the kiln during the restart.

5. The ledge on No. 4 cyclone is cleaned during any scheduled stops (for other purposes) of about 4 hours or more. This was first done on 28 November '75, and there was a large build-up. On 26 Jan. '76 the build-up was much smaller, and on 15 June 1976 (after physical modification No. 6) there was no build-up.

The Works Manager believes that the most significant physical modifications made were numbers 1 and 7, and that the most time-saving operational change is No. 2 - there have been no major chokes since this was introduced.

TABLE 7

Analyses of Various Materials

Constituents	Kiln feed	Clinker	Filter Dust		Riser * Pipe	Cyclone ** Fins
			(1)	(2)		
	%	%	%	%	%	%
SiO_2	14,0	21,3	14,7	15,1	13,7	13,4
Al_2O_3	2,8	5,7	4,2	4,5	3,8	4,0
Fe_2O_3	1,8	3,7	2,8	2,9	1,7	2,2
CaO	43,0	65,2	40,1	39,4	39,4	45,8
SO_3	0,7	0,9	1,5	1,7	12,2	2,8
K_2O	0,8	1,0	1,4	1,4	2,9	16,6
MgO	0,9	1,8	1,0	1,0	0,9	2,8
Na_2O	0,3	0,2	n.a.	n.a.	n.a.	5,4
Cl	0,02	0,002	0,18	0,19	n.a.	1,0
Loss on ign.	34,5	0,3	n.a.	n.a.	n.a.	5,9

* A porous, fairly hard, greyish material removed from the riser pipe on 11.2.75. Note the high SO_3 content.

**On 28th November 1975 the top side door on No. 4 riser pipe was opened for inspection. A build-up consisting of soft material and hard coating in the form of fins was found in the top of the cyclone. These fins were removed and a portion analysed, Note the high alkali content.

TABLE 8

Summary of Cyclone Chokes

Choke Number	Date	Time	Length of Stop hours	Cyclone Number	Clinker Production Rate tonnes/day	Weeks after firing up kiln	Kiln stop prior to choke			Time between kiln start and cyclone choke hours
							Date	Time	Reason for priorstop	
1	25-7-74	17.00	28,5	3	-	5	25-7-74	16 30	Feed trip	0,5
2	18-9-74	10.55	29,5	4	-	13	18-9-74	09 45	Feed trip	1,0
3	20-11-74	17.25	112,0	2 & 3	1296	22	20-11-74	13 43	Exhaust fan trip	3,5
4	30-11-74	16.18	18,5	4	1100	23	28-11-74	11 50	Feed trip	+12
5	2-1-75	01.25	24,0	4	1310	28	1-1-75	17 25	Clinker dragchain choke	4,5
6	4-1-75	23,30	1,5	4	1240	28	4-1-75	23 00	Exhaust fan trip	0,1
7	11-1-75	07.00	9,5	4	1200	29	11-1-75	01 03	Feed trip	5,0
8	29-1-75	01.30	10,0	4	1100	32	28-1-75	20 25	Power dip	4,0
9	3-2-75	20.30	27,0	4	1060	33	1-2-75	22 50	Power dip	+12
10	5-2-75	02.35	1,75	4	960	33	3-2-75	20 30	Cyclone choke	3,0
11	10-2-75	08.30	13,0	4	1080	34	5-2-75	02.35	Previous choke	+12
12	4-3-75	08.55	11,0	4	1010	37	26-2-75	02 15	Coal screw failure	+12
13	17-9-75	23.30	7,75	3	970	22	15-9-75	14 45	Feed trip	+12
14	18-9-75	16.00	3,5	4	970	22	17-9-75	23 30	Previous choke	9,0
14(a)	18-9-75	19.55	1,25	4	970	22	18-9-75	16 00	Previous choke	0,5
15	3-11-75	01.35	2,5	4	1130	29	31-9-75	17 25	Power dip	+12

TABLE 8 continued

Summary of Cyclone Chokes

Choke Number	Date	Time	Length of Stop hours	Cyclone Number	Clinker Production Rate tonnes/day	Weeks after firing up kiln	Kiln stop prior to choke			Time between kiln start and cyclone choke hours
							Date	Time	Reason for priorstop	
16	3-11-75	06.20	6,25	4	-	29	3-11-75	01.35	Previous choke	2,2
16a	3-11-75	12.55	11,5	3	-	29	3-11-75	06.20	Previous choke	0,25
16b	4-11-75	00.34	0,75	3	-	29	3-11-75	12.55	Previous choke	0,1
17	10-11-75	01.55	2,0	3	900	30	9-11-75	14.05	Power trip	12,0
17a	10-11-75	01.25	1,75	2	900	30	10-11-75	01.55	Previous choke	0,5
18	13-12-75	05.45	2,5	1	967	34	13-12-75	04.00	Dust transport overloaded	0,75
18a	13-12-75	00.25	0,5	1	-	34	13-12-75	05.45	Cyclone choke	1,0
19	21-12-75	09.42	5,0	3	980	36	18-12-75	17.10	Kiln feed control fault	+12
19a	21-12-75	15.30	14,25	3	-	36	21-12-75	09.42	Cyclone choke	0,75
20	26-12-75	08.25	16,25	3	980	36	26-12-75	07.52	Power trips	0,2
21	27-12-75	07.20	0,3	3	810	36	27-12-75	06.15	Clinker transport trip	0,2
22	1-1-76	12.00	0,25	3	980	37	1-1-76	11.20	Firing fan trip	0,3
22a	1-1-76	12.53	1,0	3	980	37	1-1-76	12.13	Cyclone choke	0,2
23	10-4-76	11.28	6,25	3	600	0	10-4-76	-	Kiln start up	10,5
24	16-4-76	06.45	2,5	2	1080	0	15-4-76	21.45	Power trip	2,3
25	28-4-76	11.50	2,8	3	1279	2	28-4-76	10.26	Cooler repair	0,25
-	16-8-76	-	-	-	1050	18	-	-	-	-

CHLORIDE CYCLE

Although the chloride content of our raw materials is relatively low, a high concentration does build up in some areas of the kiln. This is illustrated (in round figures) in Figure 1. Chlorides, however, are not considered to be a major problem.

TABLE 9

Chloride concentrations

Material	Date	Chloride content
Raw meal ex mill	Dec. 1975	74 ppm
" " " "	Jan. 1976	69 "
" " " "	Feb. 1976	67 "
Kiln feed ex silo	Jan. 1976	71 "
Raw water	-	79 "
Clinker	Jan. 1976	28 "
"	" "	22 "
"	Feb. "	18 "
"	" "	29 "

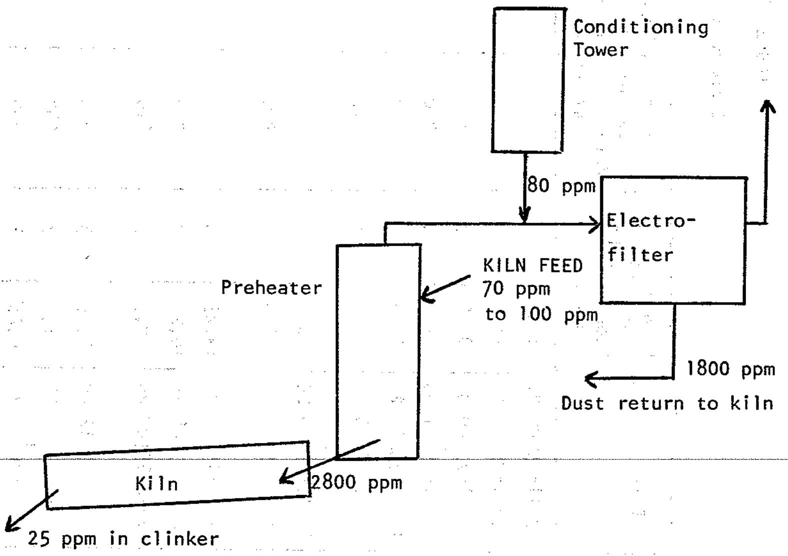

FIG. 1
Approximate chloride concentrations

CONCLUSION

Table 8 has been of assistance in developing measures to prevent chokes, or at least to reduce their severity.

On two occasions the main trouble commenced 22 weeks after firing-up the kiln - i.e. 22 weeks after starting with cyclones free from build-ups. Thereafter most cyclone chokes were associated with kiln stops (where more than 12 hours had elapsed since the previous stop it was not considered relevant). This led (a) to physical modification No. 1 - which seemed to push most of the chokes from No. 4 cyclone up to No. 3 cyclone, and this in turn led to modification No. 7. This splash plate (to "splash" the feed into the riser pipe leading to No. 4) is situated at the bottom of a long vertical duct from cyclone No. 3. As long as the material keeps flowing there is no trouble, but during a stop it seems to harden up and/or become sticky, so that it no longer flows freely, and therefore chokes up No. 3 cyclone. Operating the air jets for about an hour after each stop seems to prevent this.

It is now 18 weeks since firing up the kiln (with clean cyclones) for the third time - and we are all awaiting the 22nd week with hopeful interest!

Acknowledgements

My thanks to the Management and Staff of the Cape Portland Cement Company - particularly the Manager Chemical Services and the Works Chemist De Hoek - from whose various reports I have "borrowed" considerably.

ALKALI REDUCTION IN CEMENT KILNS

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ABSTRACT

Comparison is made between the wet and dry processing plants for cement manufacture. Typical alkali reduction capabilities for various kiln systems are given and dry process kilns with energy efficient preheater systems are seen to produce clinker with higher alkali contents than normal for older systems wet or dry. Modern calcining technology has made construction of efficient bypass systems possible which allow alkali reduction. These systems may be used in combination with energy efficient dry process kilns.

Alkalies in Cement Raw Materials, Production Processes and Alkali Reduction Systems

Introduction

Alkalies in Portland Cement have drawn attention over the last two decades due to a combination of factors:-

1. Changes in cement plant technology
2. Energy Conservation
3. Environmental compatability
4. Alkali-silica reactions in concrete

The development in cement plant technology has been a continuous change from wet to dry process owing to the superior energy efficiency of modern dry process kilns. Steeply increasing fuel prices over the past couple of years has accentuated this trend.

Calls for pollution control by the modern society are being met by installation of dust precipitators with collection efficiencies exceeding 99.5 %. As a consequence, the alkalies from cement raw materials increasingly tend to end up in the cement. Due to their volatility at sintering temperature, they circulate in the process, particularly in the kiln system, and may cause clogging problems in gas ducts and cyclones.

In the same two decades it has been established that harmfull reactions occur between cement alkalies and certain types of aggregate. Fortunately these types of aggregate though widespread are not encountered everywhere.

Alkalies in cement do, however, offer some advantages, viz.

1. Improved nodulization of clinker in the kiln
2. Higher earlier strength of the cement

Both are of some importance for the cement manufacturer.

Production Processes

Although the greater part of new cement plants to-day are employing the dry process, many wet plants are still in operation and will be in production for years ahead. Typical flow-sheets are seen on fig. 1 and 2.

When a reduction of the alkali content of the cement is required, this must generally be performed by modifying the kiln section of the plant. That is apart from the fairly rare cases where supply of alternative low-alkali raw materials can be obtained.

Fig. 3 shows the principal types of traditional cement kilns. The capacity of FLS-kilns sold between 1960 and 1974, divided up according to kiln type, is given on fig. 4. The trend has clearly been towards the energy efficient dry process, which since 1974 constitutes more than 90 % of our sale of kiln capacity. A continuation of this trend (see also fig. 5) is likely to result in a world production capacity distribution approaching one quarter wet and 3 quarters dry process by 1985 (see fig. 6).

However the consumer must pay attention to the existing plants, as they supply the cement he is using to-day. In the U. S. A. some 60 % of all kilns are of the wet type and 30 % are more than 40 years old. The dry process plants in the U. S. A. are dominated by long kilns (85 %) and 20 % are 40 years old or more. This picture will change as 90 % of the planned dry process installations will be of the cyclone preheater type.

Alkali Reduction in Kiln Systems

A sizeable portion of the alkalies are evaporated in the kiln owing to their relatively high vapor pressure at the sintering temperature (see fig. 7). Part of the alkalies is caught and recycled from the colder parts of the kiln, preheater, filtre and raw mill - if the smoke gasses are utilized for drying of raw materials. Repeated evaporation and condensation results in an increasing internal circulation, until equilibrium is reached, whereby the system gives off the same quantity of alkalies as contained in the kiln feed.

The kiln systems vary with regard to alkali trapping efficiency, depending on the preheater and heat exchanger type (see fig. 8). In short when conserving energy - alkalies are conserved as well.

The smoke gasses are dedusted in filtres, mainly electrostatic precipitators. The composition of dust from these installations may be fairly rich in alkali for certain 'open' kiln systems, and the content of alkali in the clinker may be lowered by discard of a fine fraction of the dust.

Unfortunately this method is only effective in wet process plants, due to the dust composition (see fig. 9). Even for the wet process it is only kilns operating as so-called nodule kilns, which can employ this principle of alkali reduction. Large-diametre kilns usually operates as 'dust' kilns yielding precipitator dust with moderate contents of K_2O.

The concentration of alkali in the dust depends on whether the vapors of alkali are condensed as individual droplets or on the surface of solid particles. The latter is normal in dust-operated wet kilns, long dry kilns, and particularly in cyclone preheater kilns.

Consequently, only some (small capacity) wet plants can reduce the alkali content of clinker by rejecting precipitator dust. And filter dust disposal to-day is no easy matter due to restrictions from anti-pollution authorities. One way to overcome this problem is to leach the dust with water and recycle the alkali-free slurry to the kiln. The dissolved alkalies in the effluent from such a plant (see fig. 10) gives a strongly alkaline reaction and may require neutralization with acid before disposal. Also a leaching plant costs money to construct and operate, and the leached slurry, when added to the kiln slurry, often results in a higher overall water content in the kiln feed.

In the 4-stage preheater kiln a certain reduction of the alkali content can be made by means of a so-called by-pass (see fig. 11). The by-pass is unfortunately a capital demanding installation, and it increases the fuel expenditure. Actually most by-pass installations are made for chloride reduction. This is due to the limited effect on the alkali content of the clinker (see fig. 12). Mainly K_2O is reduced (see fig. 13 and 14).

The heat penalty incurred due to the alkali by-pass is quite heavy (see fig. 15) and the producers are generally not tempted to install such equipment unless compelled to for production reasons, viz. serious clogging problems arising when the clinker alkali content exceeds approx. 2 %. Disposal of dust is again a problem with by-pass operation.

Advanced Kiln Systems

The development of calcining systems in recent years has been directed towards 3 main objects, viz.

1. Reduction of the installation cost of kilns compared with the 4-stage preheater system
2. Production capacities up to 10 000 mtpd on moderate diametre kilns
3. Improved by-pass efficiency combined with an energy efficient dry process kiln

The new kiln systems we have developed (see enclosures No. 1, 2 and 3) and their application with regard to cost, capacity and alkali reduction is shown on fig. 16.

For outputs up to approx. 4500 mtpd. integral calcining kilns (see fig. 17), with calcining in suspension at the kiln inlet, are the most inexpensive of all commercial rotary kiln systems. A special scooping device at the kiln inlet raises the degree of calcination from a maximum of 30 % in the conventional 4-stage preheater kiln to about 50 - 60 %. The length of the kiln is consequently some 40% shorter than a 4-stage kiln. An efficient by-pass cannot be established on this kiln system, as the alkalies are extensively condensed on particulate surfaces before the kiln gasses leave the kiln.

For outputs ranging from 4500 - 10 000 mtpd the calcining kiln with separate calciner and hot air pipe from the clinker cooler is the only system that will will give a reasonable kiln diametre. This kiln system employs a supply of only 30 % of the fuel in the kiln proper, compared with 100 % in the 4-stage kiln. Hence alkalies evaporated in the sintering zone are concentrated in a much smaller volume of gasses, and a by-pass will be 3 times as efficient compared with systems where all gasses are drawn through the kiln. Or - the heat penalty will be considerably less. (See fig. 18)

We have developed a special version of this system (see fig. 19) for raw materials with high contents of volatile matter or for maximum alkali reduction. In this system all gasses leaving the kiln are extracted from the system, whereby the biggest possible alkali drain is established. The heat penalty is 100 - 150 kcal/kg clinker, including the heat of evaporation of alkali compounds, which could for example amount to 40 kcal/kg clinker. The heat loss is also dependent on the dust lost from the by-pass, which is quite low due to the relatively low gas velocity at the kiln inlet and the high degree of calcination of the raw meal.

In cases where a large and variable by-pass is required, for example 0 - 100 %, the gas ducts are arranged as indicated on fig. 20. A large kiln of this type produces ordinary Portland clinker at approx. 750 kcal/kg and low-alkali clinker at 850 - 900 kcal/kg clinker, with a 100 % by-pass.

Conclusion

Typical alkali reduction capabilities for various kiln systems are given on fig. 21. It is clearly seen that conventional dry process kilns with energy efficient preheater systems produce clinker with higher alkali contents than normal for older systems, wet or dry. By-pass installations may be used for alkali reduction, but are not normal to-day due to extra costs of installation, higher fuel consumption and relatively low efficiency. Modern calcining technology, however, has made construction of highly efficient, low-energy-loss by-pass systems possible in combination with energy efficient dry process kilns.

The trend, however, will undoubtedly continue towards higher alkali contents in cement due to the gradual close-down of small scale factories wet or dry, operating with inferior economy compared with large dry process facilities. (See fig. 22). The potential alkali reducers, viz. operators of small wet kilns are generally not in a position to accept additional operating expenses for alkali reduction unless they can be passed on to the consumer.

Fig. 1

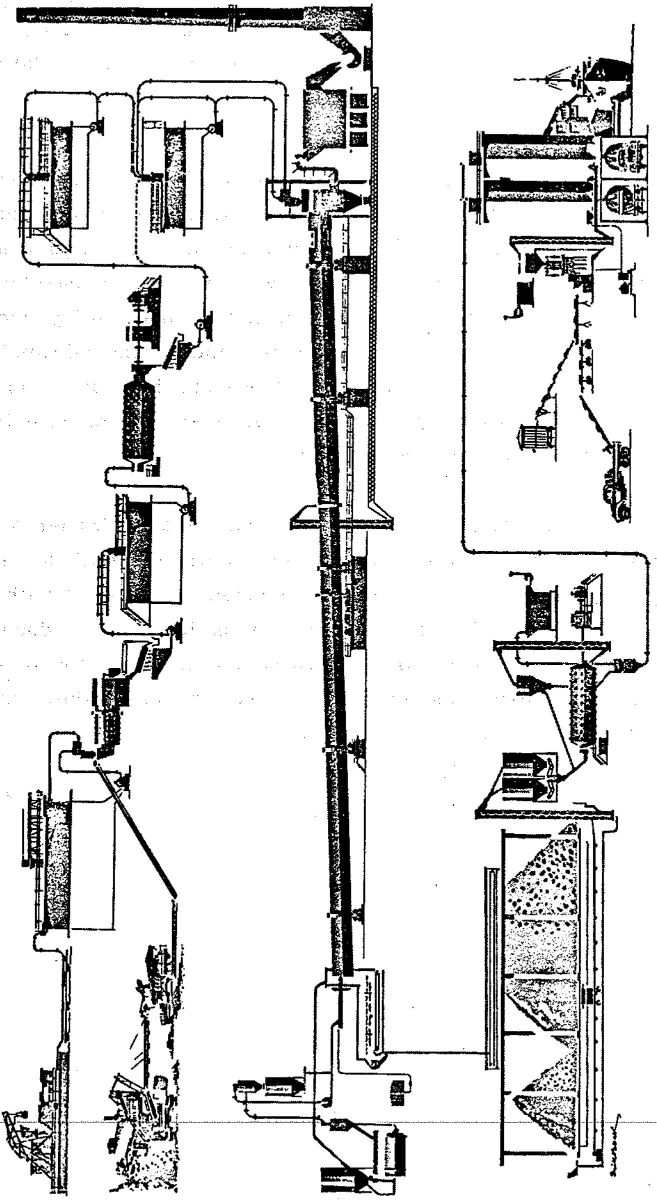


Fig. 2

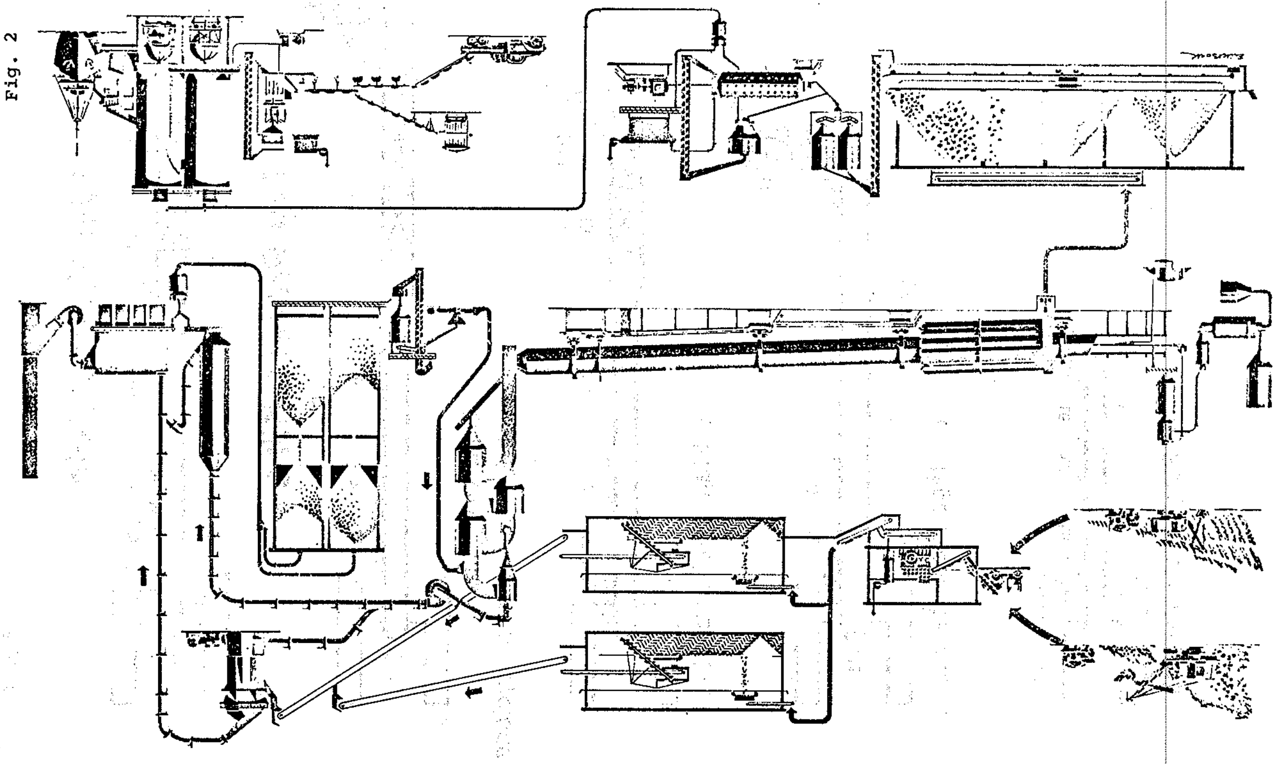
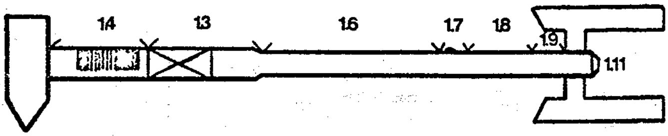
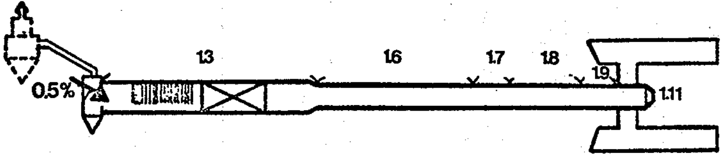


Fig. 3

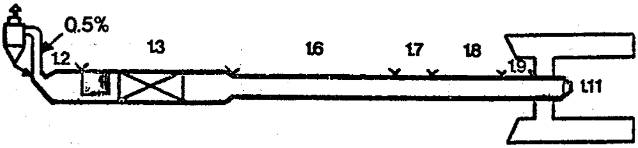
Wet Process Kiln



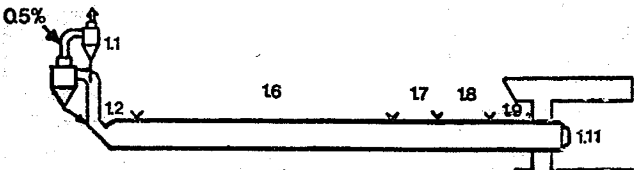
Dry Process Kilns



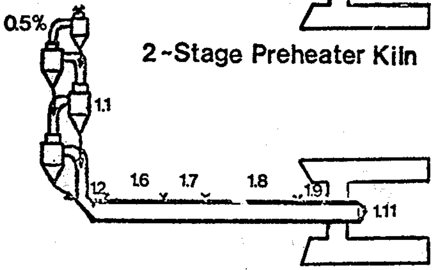
Long Dry Kiln
often with dedusting cyclone



1-Stage Preheater Kiln



2-Stage Preheater Kiln



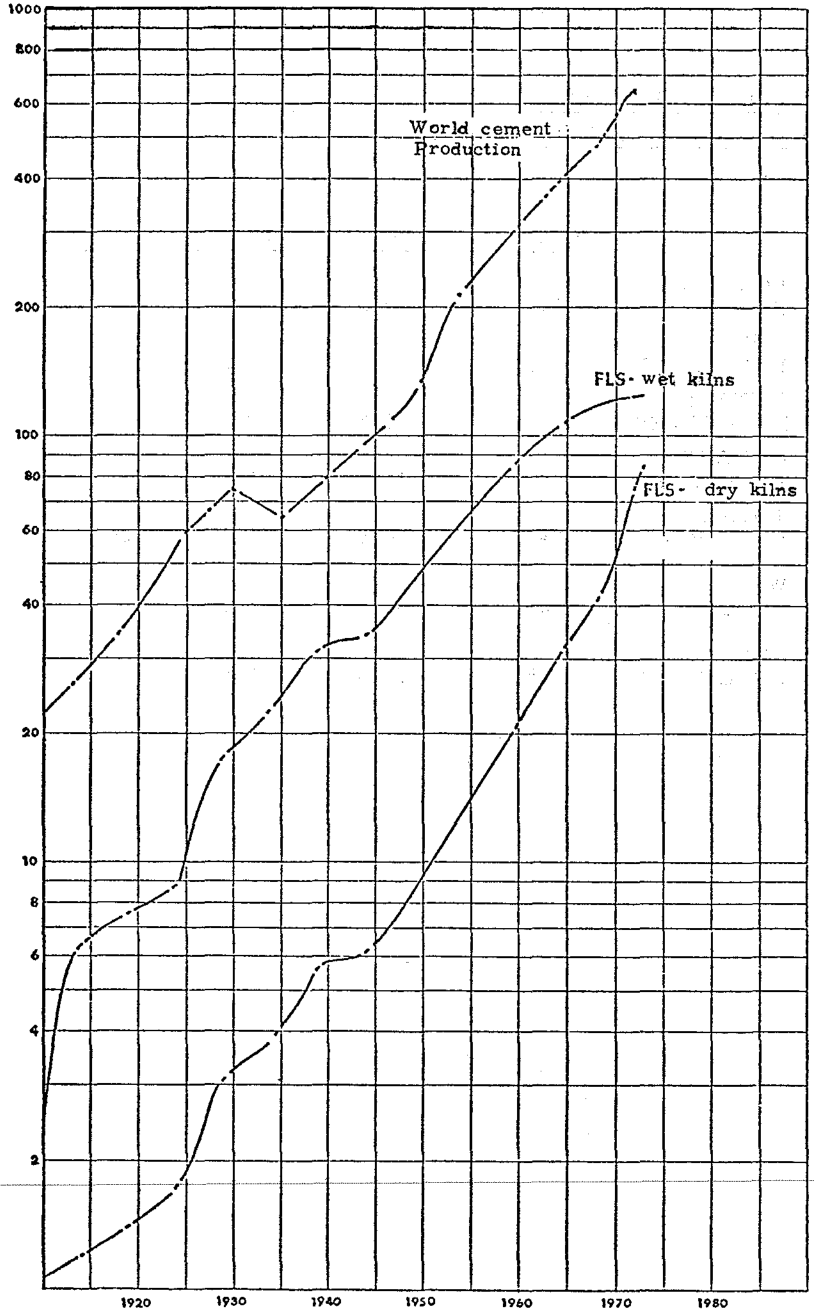
4-Stage Preheater Kiln

Fig. 4

F. L. SMIDTH KILN CAPACITY SOLD 1960 - 1974
% - DISTRIBUTION ON PROCESS

	1960 - 64	1965 - 69	1970 - 74	1975 -
LONG DRY KILN	31.7	12.3	3.1	
1-STAGE PREHEATER	0.5	18.0	3.8	
2-STAGE PREHEATER	1.9	8.5	2.1	
4-STAGE PREHEATER	0	15.7	75.6	
TOTAL DRY PROCESS	34.1	54.5	84.6	90 +
WET PROCESS	65.9	45.5	15.4	
AVERAGE KCAL/KG CL.	1250	1120	890	

Fig. 5



1000
800
600
400
200
100
80
60
40
20
10
8
6
4
2
1920
1930
1940
1950
1960
1970
1980
World cement Production
FLS- wet kilns
FLS- dry kilns

Fig. 6

CEMENT PRODUCTION FORECAST TILL 1985

	World Production	Capacity Distribution % Wet	 % Dry	Kcal/kg Cement Average
1970	573	50	50	1272
1975	700	43	57	1225
1980	840	35	65	1184
1985	1008	28	72	1138

Fig. 7

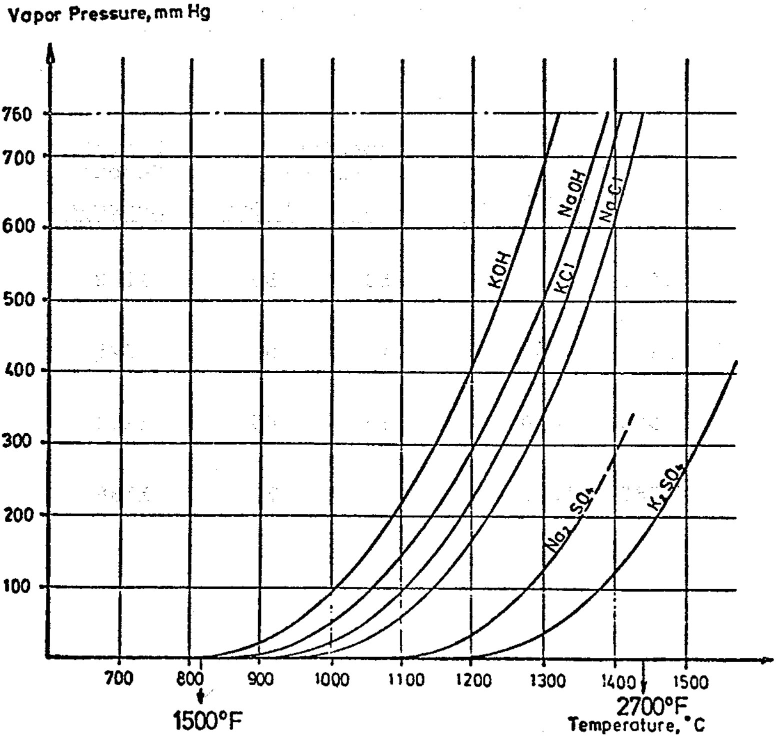

Vapor Pressure, mm Hg
760
700
600
500
400
300
200
100
700
800
900
1000
1100
1200
1300
1400
1500
1500°F
2700°F
Temperature, °C
KOH
NaOH
KCl
NaCl
Na_2SO_4
K_2SO_4

Fig. 8

DRY-PROCESS

Temperature profiles inside the kiln
and
Alkali-reduction for different kiln types

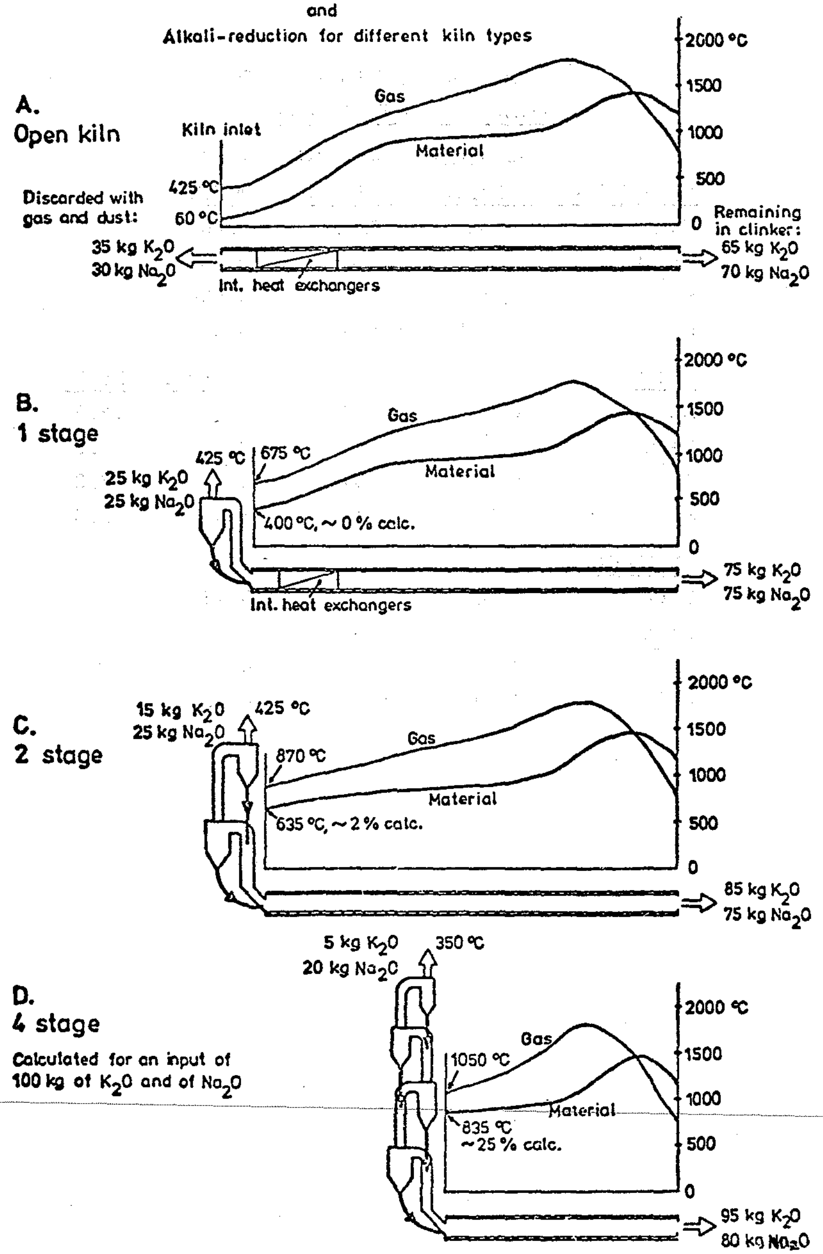


Fig. 9

ANALYSES OF DUST FROM ELECTROFILTRES ETC.

RAW MEAL	2-STAGE KILN	4-STAGE KILN	WET KILN	
K_2O	0.53	0.30	0.46	
Na_2O	-	-	0.25	
S	0.00	-	0.030	
Cl^-	0.004	0.008	0.025	
DUST			COARSE	FINE
K_2O	0.93	0.40	10.5	22.3
Na_2O	-	-	0.65	1.9
S	0.15	0.10	4.2	7.2
Cl^-	0.12	0.05	1.5	2.5
CLINKER				
K_2O	0.84	0.51	0.43	
Na_2O	-	-	0.31	
S	0.19	-	0.10	
Cl^-	0.001	0.005	0,003	

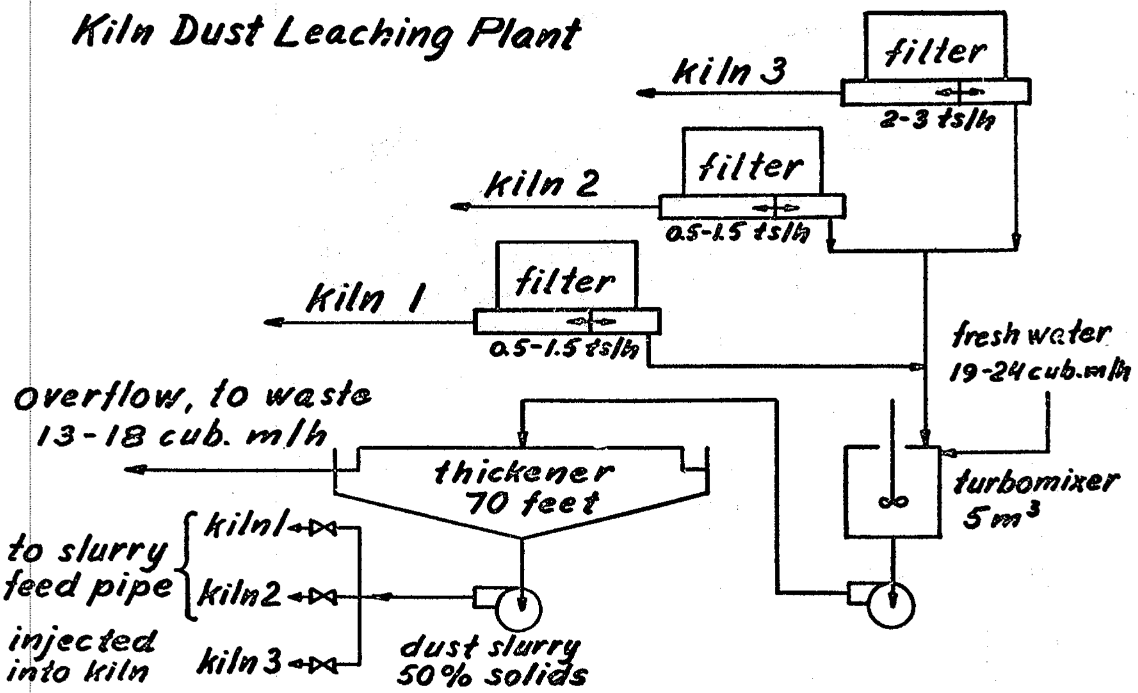

Kiln Dust Leaching Plant
filter
kiln 3
2-3 ts/h
filter
kiln 2
0.5-1.5 ts/h
filter
kiln 1
0.5-1.5 ts/h
fresh water
19-24 cub. m/h
overflow, to waste
13-18 cub. m/h
thickener
70 feet
turbomixer
5 m³
to slurry feed pipe
kiln1
kiln2
kiln3
injected into kiln
dust slurry
50% solids

Fig. 10

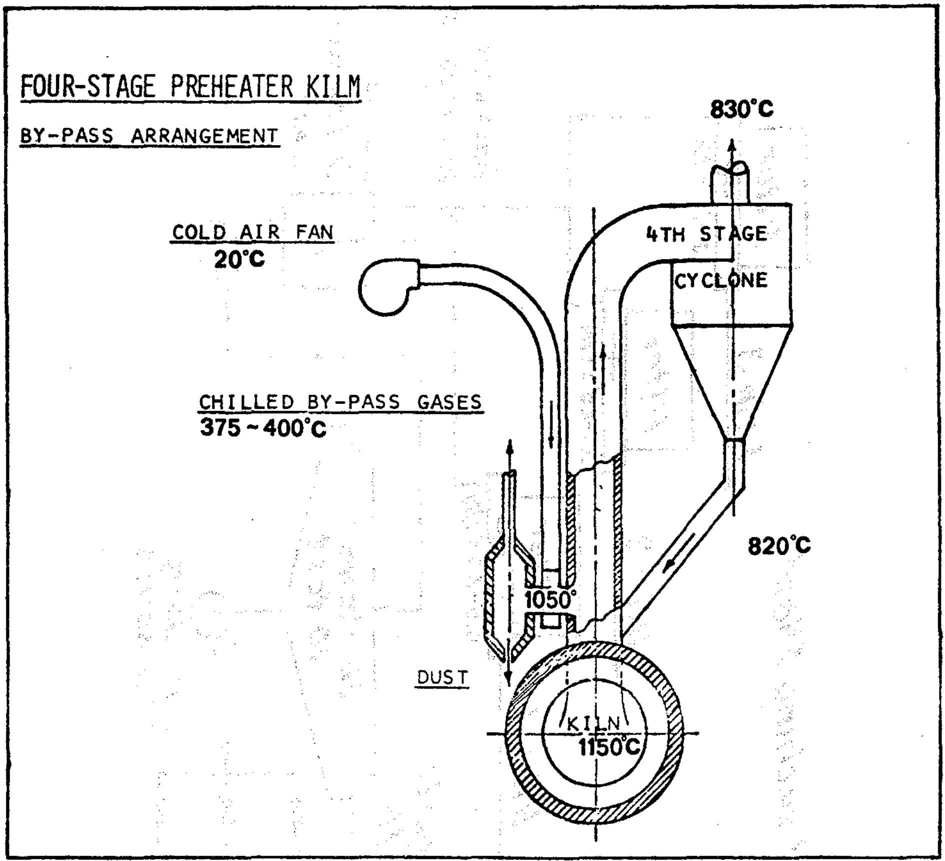
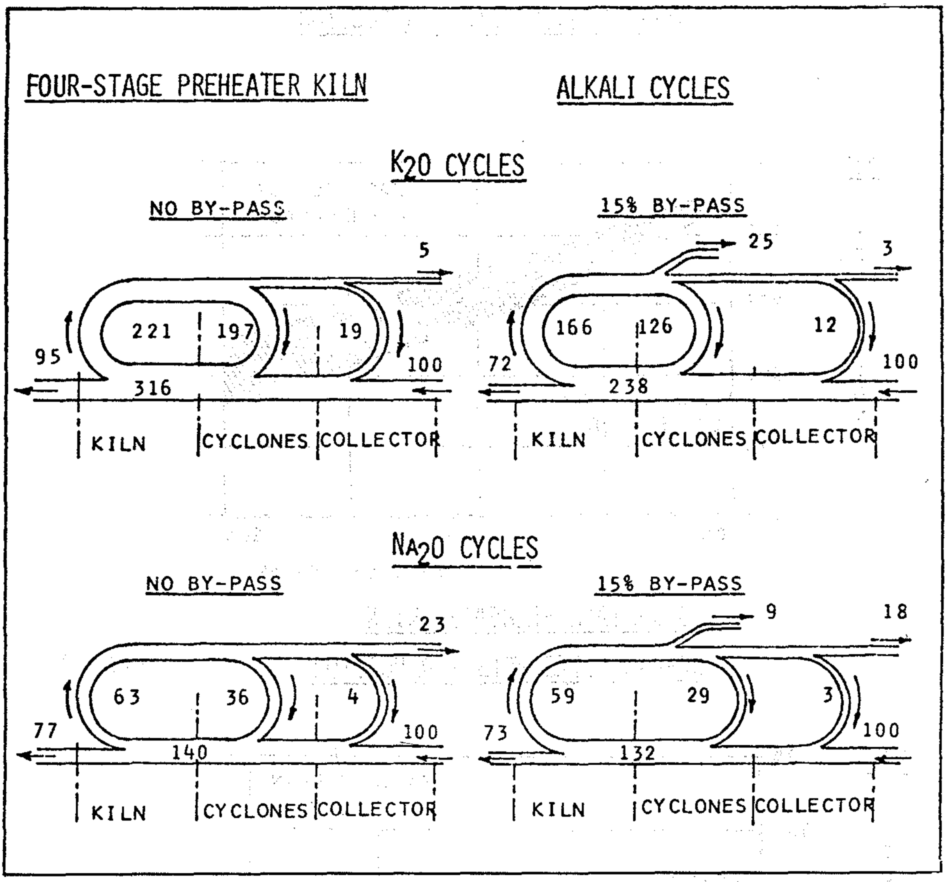
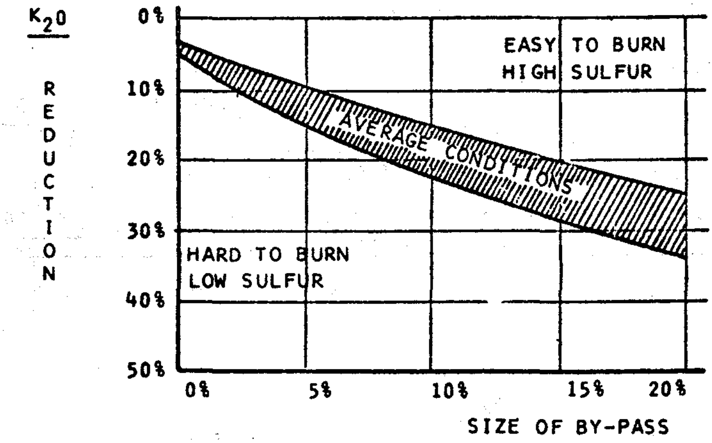

FOUR-STAGE PREHEATER KILM
BY-PASS ARRANGEMENT
830°C
COLD AIR FAN
20°C
4TH STAGE
CYCLONE
CHILLED BY-PASS GASES
375 ~ 400°C
820°C
1050°
DUST
KILN
1150°C

Fig. 12


FOUR-STAGE PREHEATER KILN
ALKALI CYCLES
K2O CYCLES
NO BY-PASS
5
221
197
19
95
100
316
KILN
CYCLONES
COLLECTOR
15% BY-PASS
25
3
166
126
12
72
100
238
KILN
CYCLONES
COLLECTOR
NA2O CYCLES
NO BY-PASS
23
63
36
4
77
100
140
KILN
CYCLONES
COLLECTOR
15% BY-PASS
9
18
59
29
3
73
100
132
KILN
CYCLONES
COLLECTOR

FOUR-STAGE PREHEATER KILN
BY-PASS SIZE VERSUS REDUCTION

Fig. 13



FOUR-STAGE PREHEATER KILN
BY-PASS SIZE VERSUS REDUCTION

Fig. 14

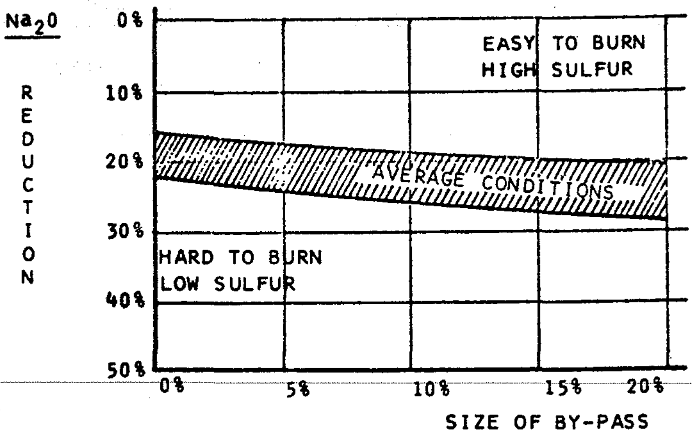


Fig. 15

FOUR STAGE PREHEATER KILN

K_2O-REDUCTION VERSUS EXTRA FUEL EXPENSES

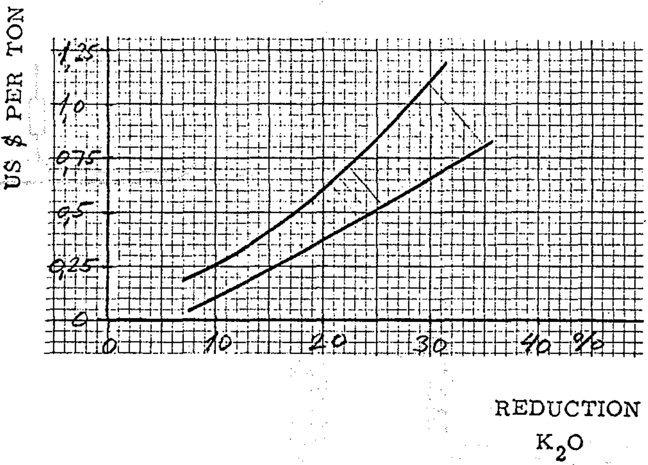


Fig. 16

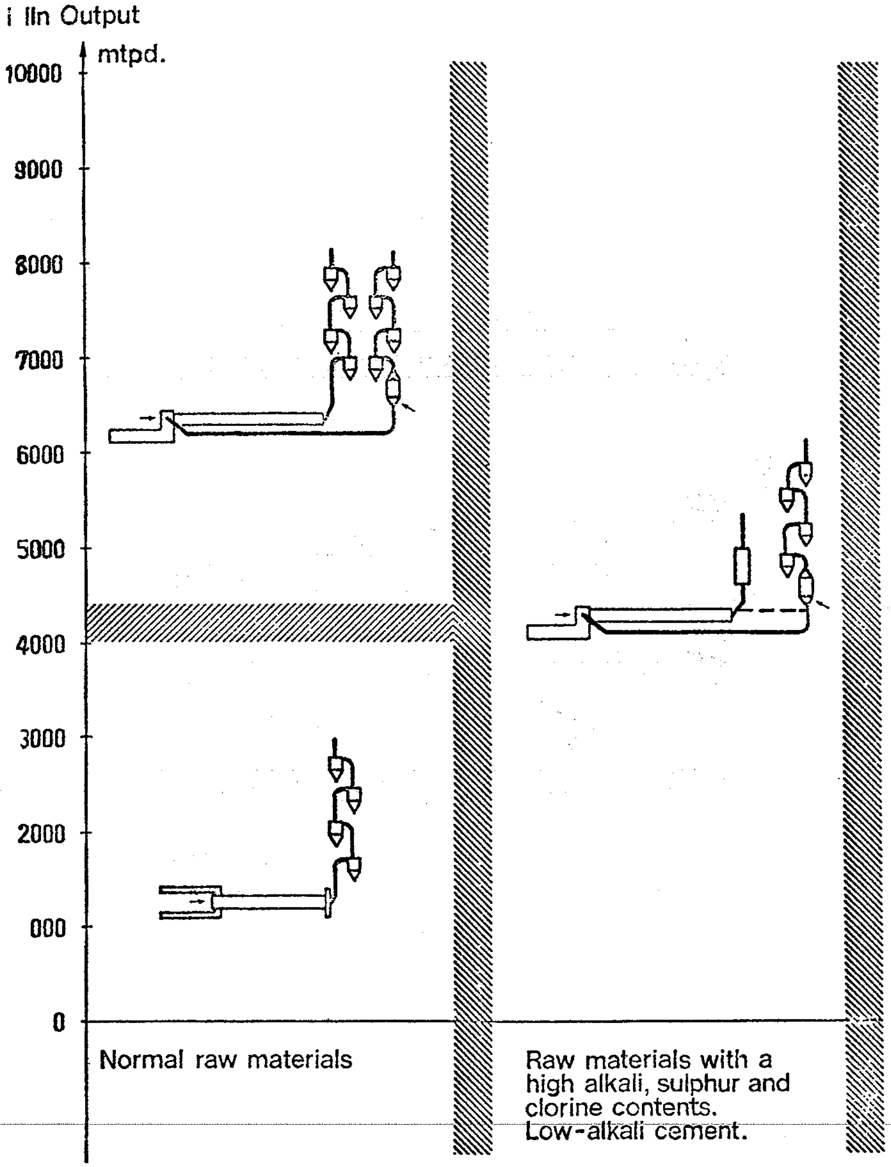
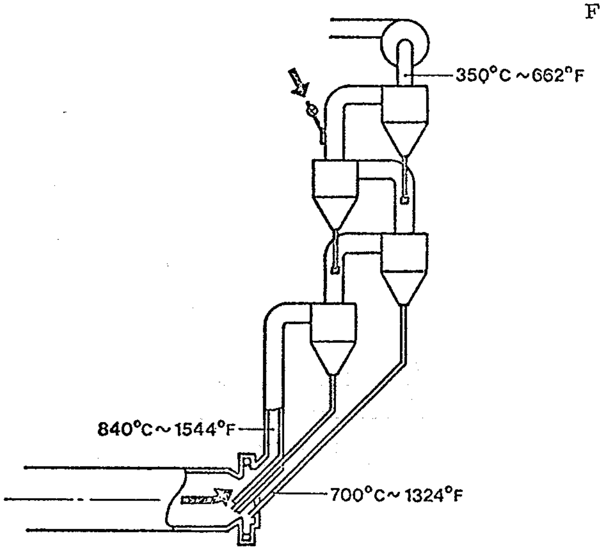

iln Output
mtpd.
10000
9000
8000
7000
6000
5000
4000
3000
2000
000
0
Normal raw materials
Raw materials with a high alkali, sulphur and clorine contents.
Low-alkali cement.

Fig. 17



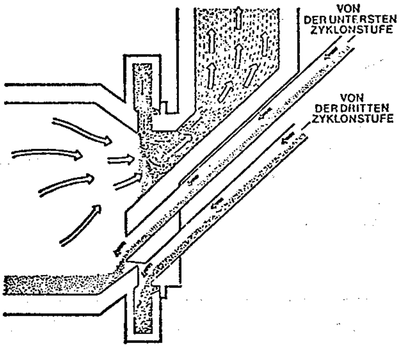


Bild 8: Kalzinierung im Ofeneinlauf mit getrennter Mehlzufuhr von der 3. und der 4. Zyklonstufe

Calcining in the kiln inlet with separate feed of meal from the third and the fourth cyclone stage

Fig. 18

F. L. SMIDTH & CO. A/S

CALCINER KILN BYPASS

% K_2O REDUCTION IN CLINKER.

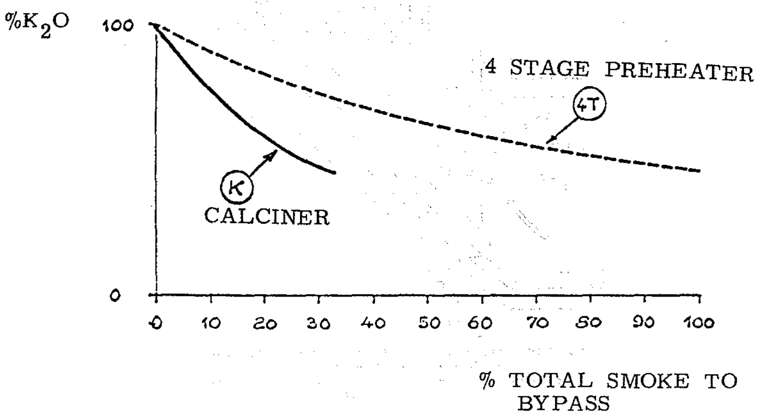


Fig. 19

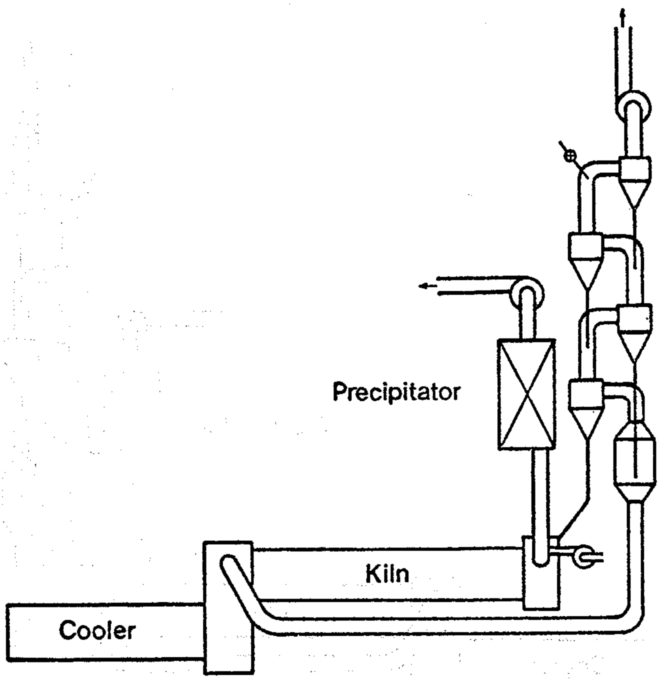


Fig. 20

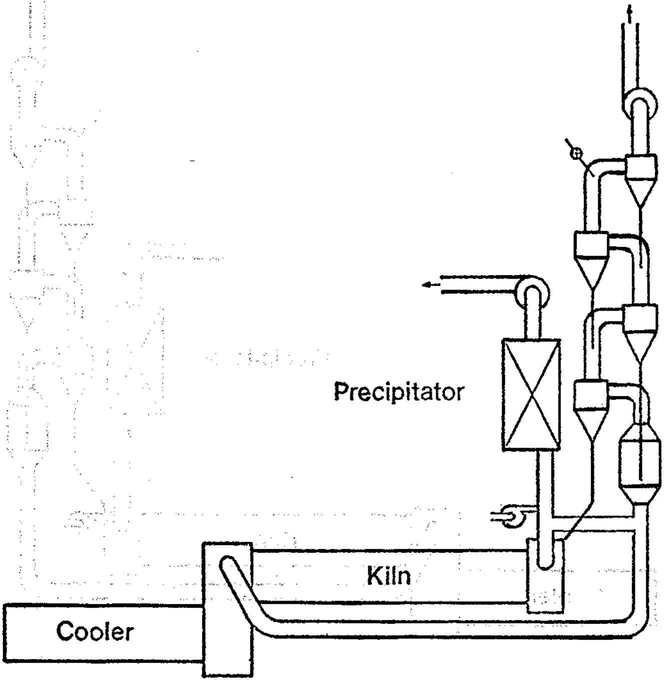
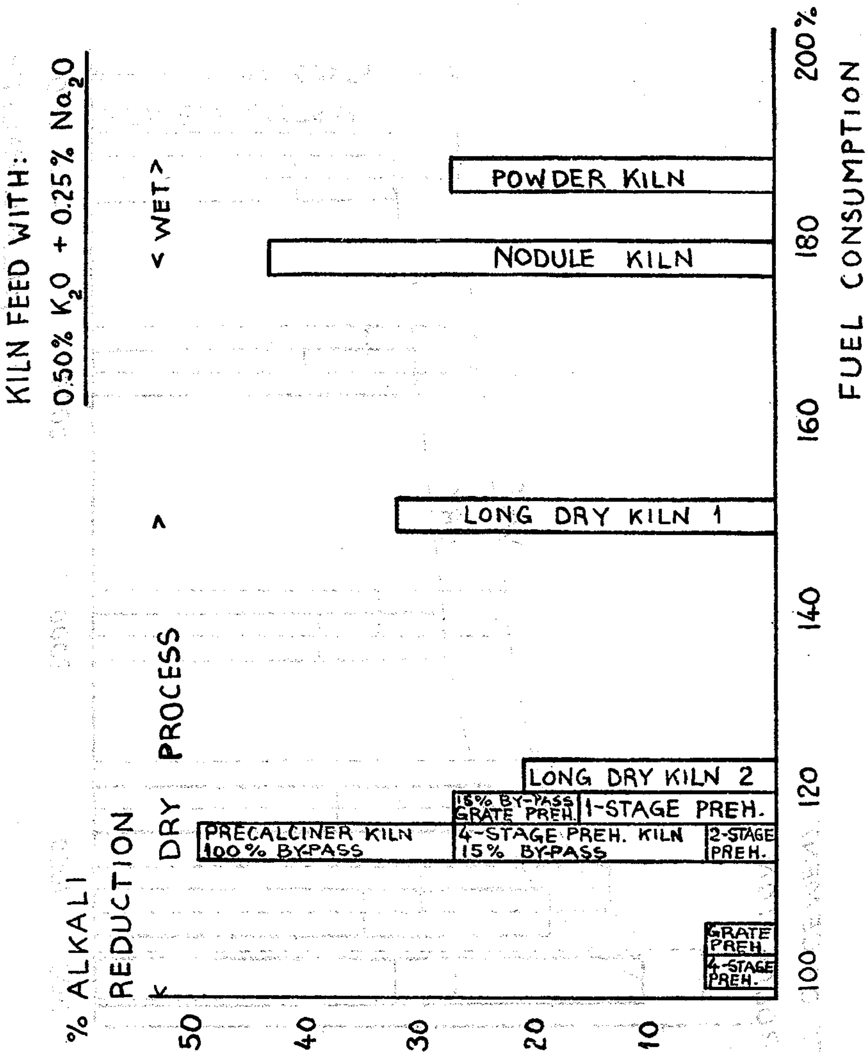
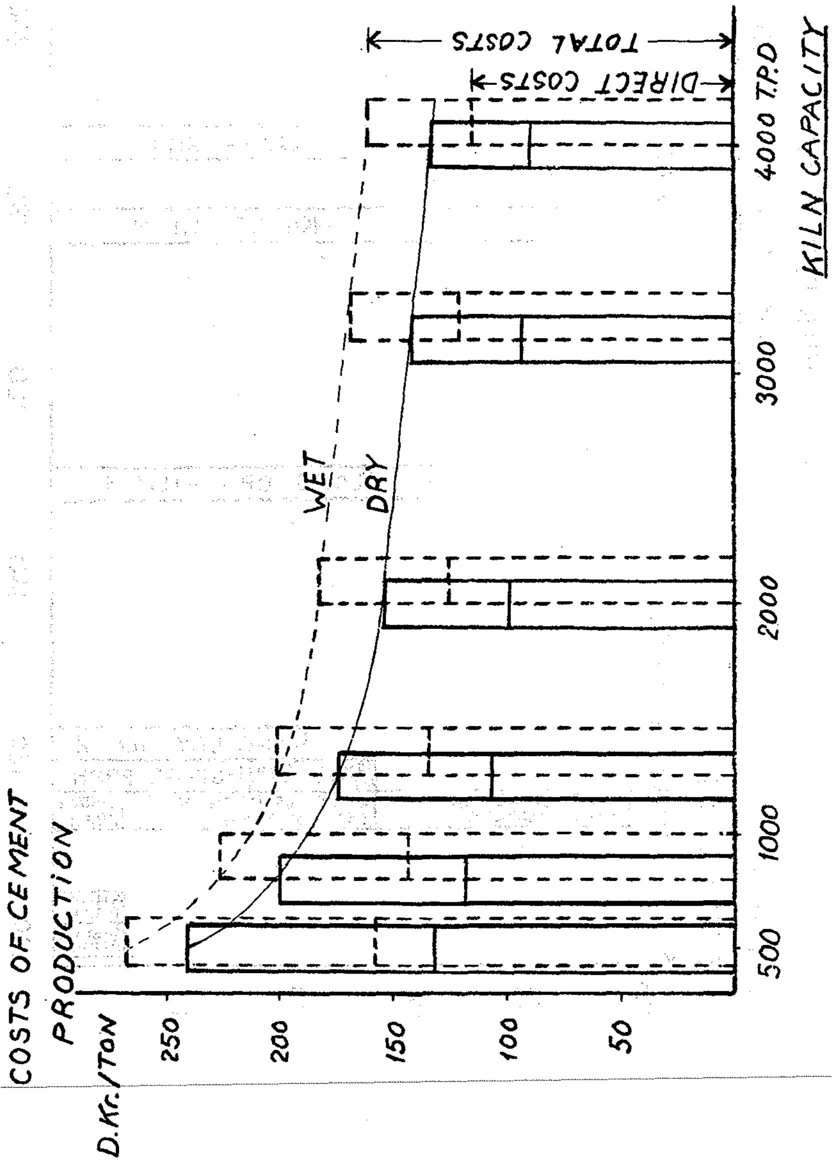


Fig. 21



KILN FEED WITH:
0.50% K₂O + 0.25% Na₂O
< WET >
< DRY PROCESS >
% ALKALI REDUCTION
50
40
30
20
10
FUEL CONSUMPTION
100
120
140
160
180
200%
POWDER KILN
NODULE KILN
LONG DRY KILN 1
LONG DRY KILN 2
15% BY-PASS GRATE PREH.
1-STAGE PREH.
PRECALCINER KILN 100% BY-PASS
4-STAGE PREH. KILN 15% BY-PASS
2-STAGE PREH.
GRATE PREH.
4-STAGE PREH.

Fig. 22


COSTS OF CEMENT PRODUCTION
D.Kr./TON
250
200
150
100
50
500
1000
2000
3000
4000 T.P.D
KILN CAPACITY
WET
DRY
TOTAL COSTS
DIRECT COSTS

CONTRIBUTION TO DISCUSSION

Dr. G.M. Idorn

It is interesting to observe that the alkali contents in cements can now be rather precisely assessed according to the nature of the cement materials (the "impact" of alkalies) and the type of cement processing equipment. Since any establishment of a cement manufacturing unit is a long-term investment it should therefore be possible to identify the alkali-contents for all cements over the world, and also to foresee any short term changes which may occur when a new unit is decided upon, or long term changes by means of forecasting technique modifications.

It is also interesting to observe that the cement industry equipment maker is a long-term planner. There are less than 10 major cement manufacturer-equipment making firms in the World, managing less than 10 billion dollars of sales per year. There are more than 4 thousand cement manufacturers and hundreds of thousands of cement using companies. These latter partners in the game, and especially the cement consumers (comprising a 2-300 billion dollar annual business over the World) have hardly any coherent long term planning for their technology development. It would seem to be desirable that some body or business agglomeration should work out a framework for forecasting the wanted and possible technology development, also involving the social aspects, and the resource and energy problems. Such a forecast ought to be made available for computation with the expected development of cement manufacture and of cement manufacture equipment so as to gain a more complete pattern of future possibilities to choose among.

3. THE EFFECT OF ALKALIES IN CEMENTS AND CONCRETES

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 $\sim$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 development.

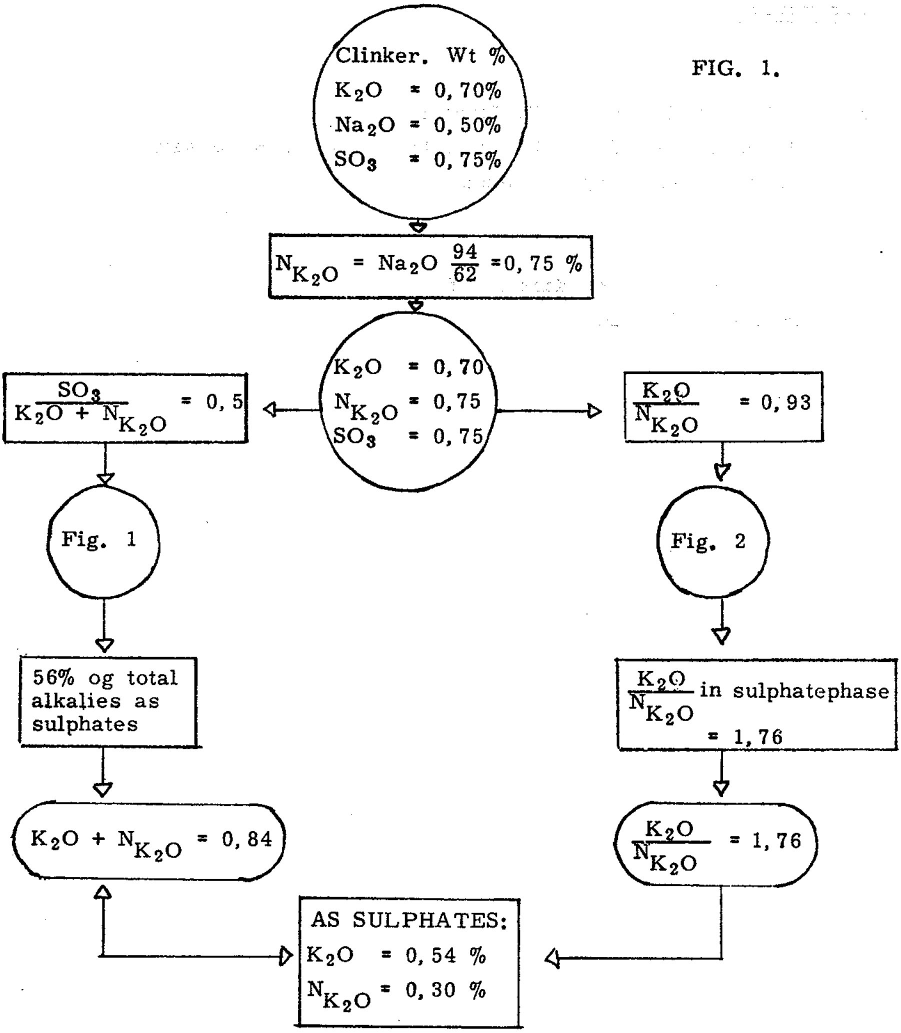
   Therefore, we will concentrate on these very early hydration processes also in relation to the physical properties of the cement particles and the reaction products.

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.



	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 %	

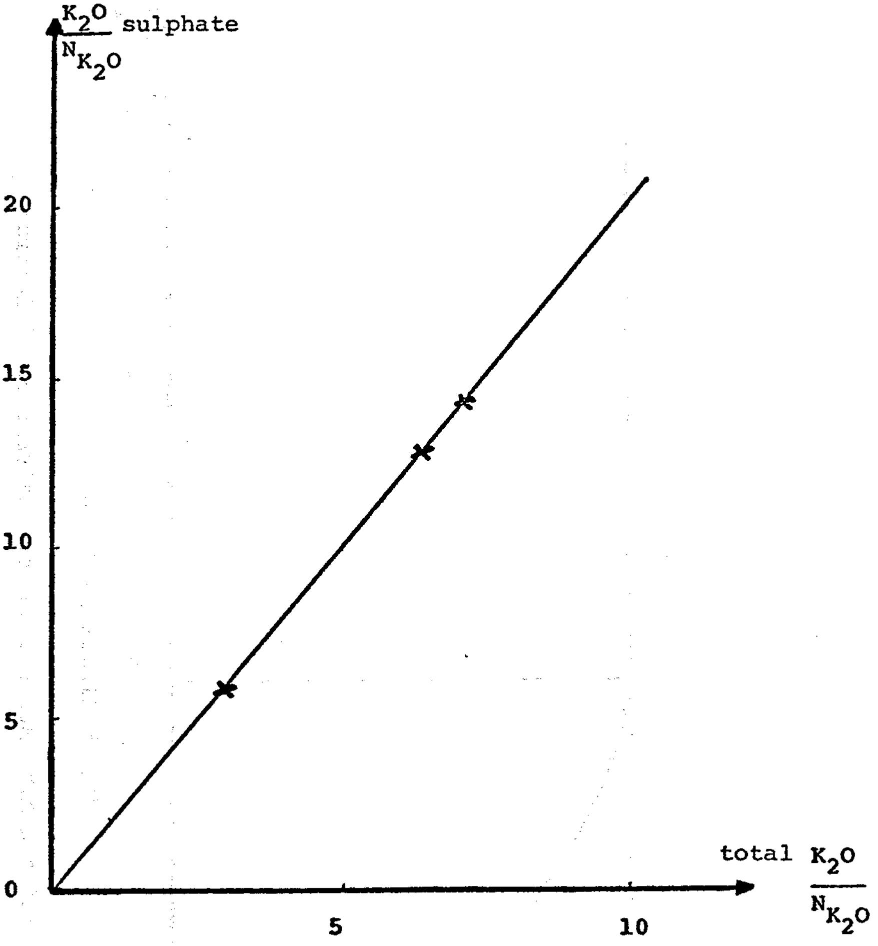


Fig. 2. : Na-K - distribution in clinker.

Data from H.W.W. Pollitt & A.W. Brown.

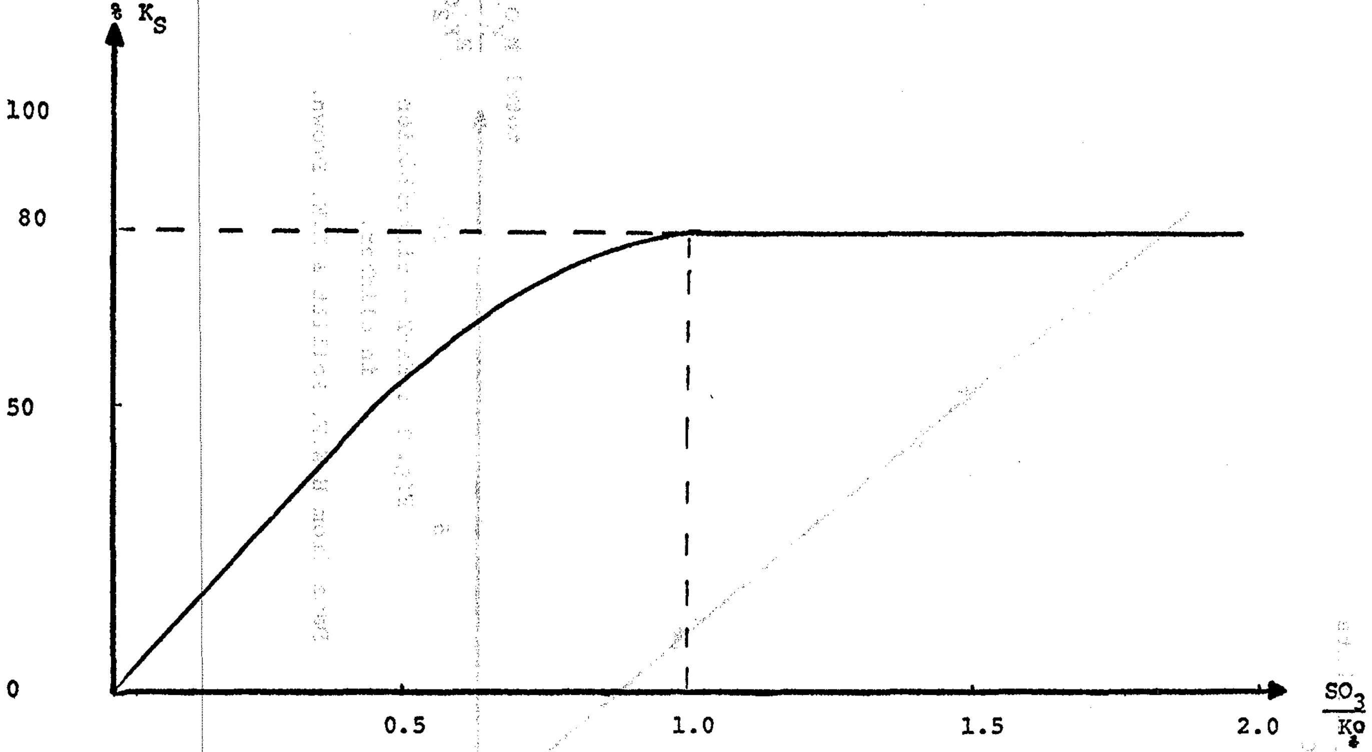


Fig. 3 Alkali as Sulphate

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_3S	44 - 77 %
LSF	88 - 99 %
SM	2,4 - 5,8
AM	0,9 - 3,5
K_2O	0,1 - 1,5 %
Na_2O	0,1 - 0,75 %
SO_3	0,1 - 2,2 %

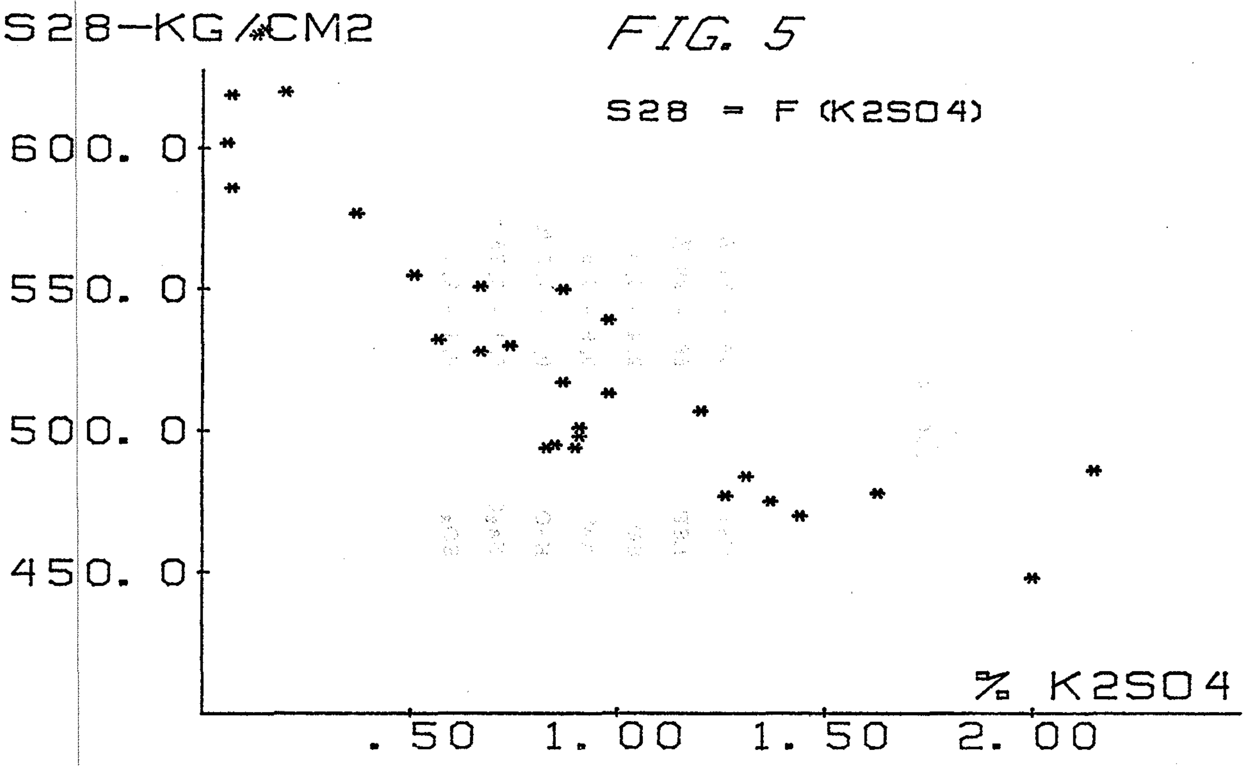


FIG. 5

FIG. 6

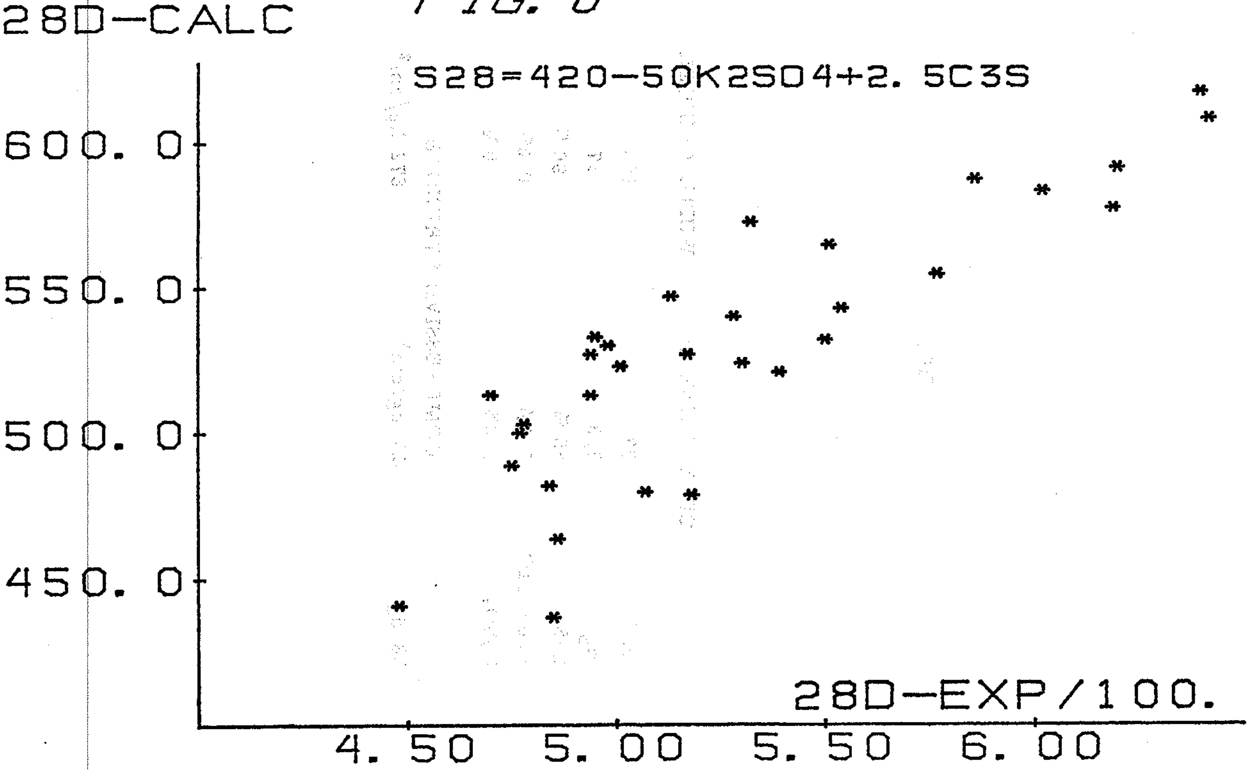

28D-CALC
S28=420-50K2SO4+2. 5C3S
600. 0
550. 0
500. 0
450. 0
28D-EXP/100.
4. 50
5. 00
5. 50
6. 00

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

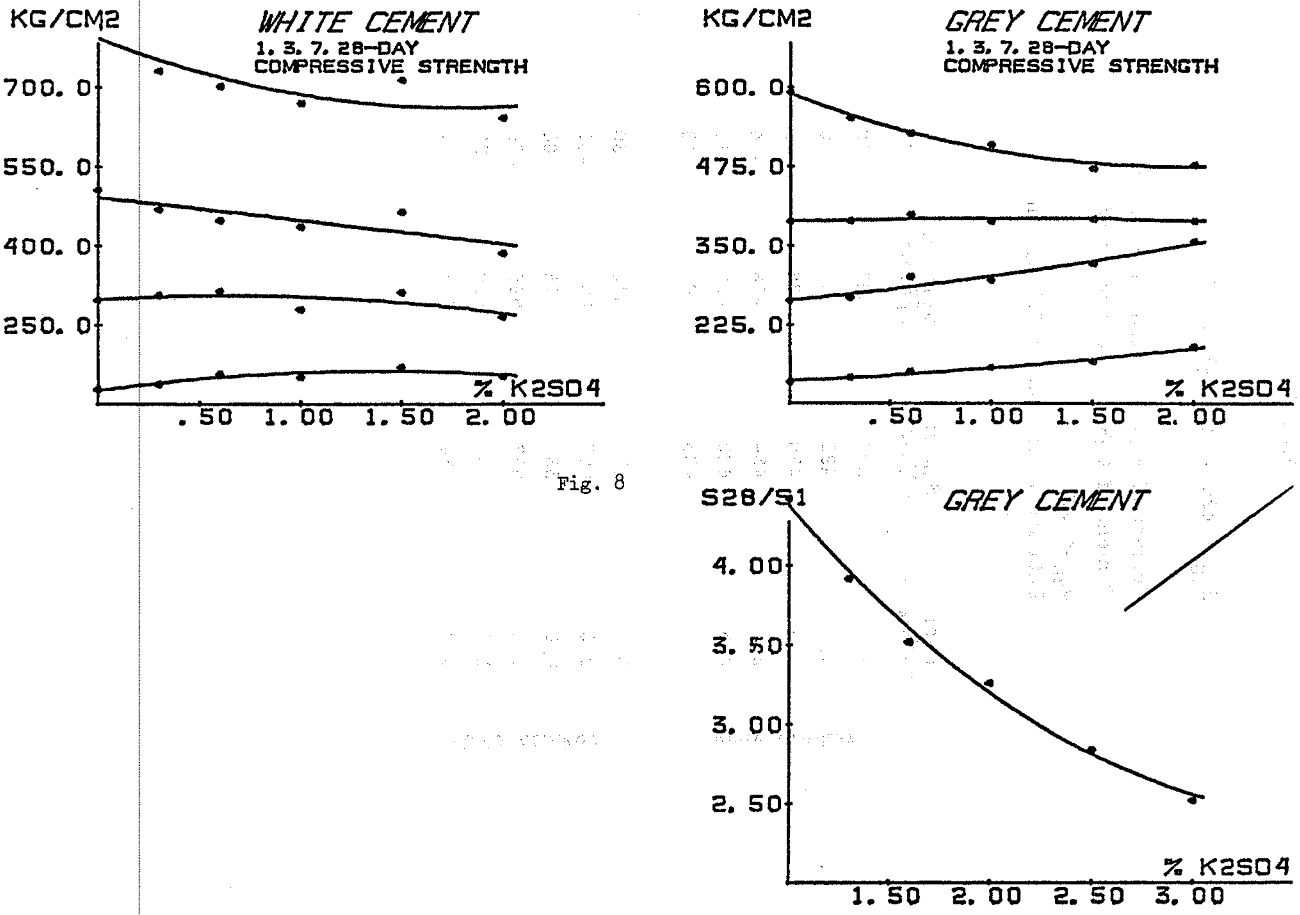

KG/CM2
WHITE CEMENT
1. 3. 7. 28-DAY
COMPRESSIVE STRENGTH
700. 0
550. 0
400. 0
250. 0
% K2SO4
.50
1. 00
1. 50
2. 00
KG/CM2
GREY CEMENT
1. 3. 7. 28-DAY
COMPRESSIVE STRENGTH
600. 0
475. 0
350. 0
225. 0
% K2SO4
.50
1. 00
1. 50
2. 00
S28/S1
GREY CEMENT
4. 00
3. 50
3. 00
2. 50
% K2SO4
1. 50
2. 00
2. 50
3. 00

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/cm²

	total K_2SO_4 %	S_{28} exp. kg/cm²	S_{28} calc. kg/cm²	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

CONTRIBUTION TO DISCUSSION

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 requirement there are, as Mr. Bryant Mather has suggested, other procedures 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

THE INFLUENCE OF ALKALI-SILICA REACTIVITY ON THE DEVELOPMENT OF TENSILE BOND STRENGTH

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ABSTRACT

The results of cement/aggregate tensile bond strength measurements are discussed in terms of the development of cement adhesion to reactive and unreactive aggregates, their temperature dependence and the alkali content of cement.

The results show that both temperature and alkalies have a marked effect on the adhesion to reactive aggregates and determine the stage at which the reactions begin to destroy further development of bond strength. It is concluded that failure at the contact in certain cases may be due to the development of a zone of weakness in the paste immediately adjacent to the interface, rather than failure at the interface itself.

Introduction

The mechanisms of paste strength development and the development of aggregate/cement adhesion appear to be areas which have not been as extensively researched as for example have the problems of hydration chemistry. And yet in many cases the bond between aggregate and cement paste forms the weakest link in the overall strength of a concrete and therefore plays an important part in the final strength of finished concrete units.

F. M. Lea[1] in The Chemistry of Cement and Concrete has reviewed the main ideas on aggregate/cement bond strength and suggests that the factors affecting bond strength are as follows:-

1. Surface Rugosity - keying to the aggregate surface.
2. Epitaxial Growth - the growth of cement hydrates aligned to crystallite lattice directions in the aggregate.
3. The enhanced cement hydration reaction rates due to increased crystal nucleation at the interface.
4. Variations in water/cement ratio at the interface leading to microscopic variations in paste strength.
5. Van der Waals forces acting across the interface.

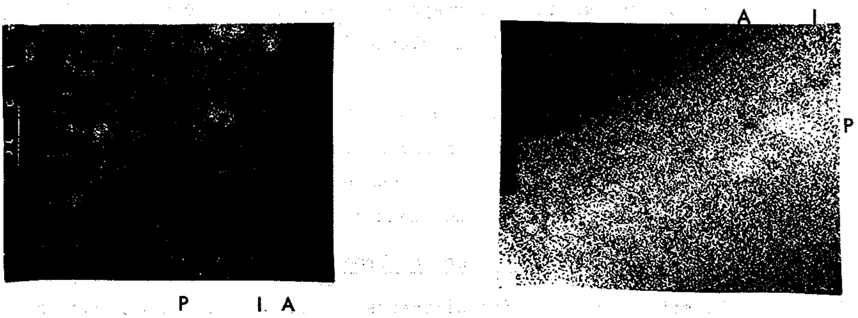
Considering these various factors it could reasonably be supposed that factor 1 would be important although it should be noted that Alexander et al.[2] after numerous experiments suggested that there is little evidence to support the view that deep pits and extensive interlocking are required at the interface before high tensile bond strength can develop. Factor 2 may also be important in that calcium silicate hydrates may well develop in alignment with silicic lattices. This is also supported by Alexander et al.[2] who, in another series of experiments found that the modulus of rupture of the aggregate/cement bond was directly related to the silica content of silicic rocks used as aggregate in his experiments. These first two, and also factors 3, 4 and 5 can play a part in modifying overall strength but to these must be added another factor, that of chemical reactivity of the aggregate surface. Many types of aggregate have been reported as being reactive. Particularly important in this category are opal, trydimite, cristobolite and chalcedonic, glassy and cryptocrystalline rocks. These materials may be reactive because their silica is crystographically disordered, as is opal, or alternatively they may be microcrystalline or microporous with a large internal surface area available for reaction. Perhaps even pure crystal quartz should be classed as reactive in that it is soluble in alkalies at high values of pH. This factor was stressed by Alexander[2] who suggested that even materials such as basalt, become reactive if finely divided and that this form of pozzolanic activity, occurring at the surface of siliceous fillers, probably also determines the characteristics of bond between normal siliceous aggregates and portland cement paste.

Experimental Procedures

The effects of reactive siliceous aggregates on bonding can be conveniently studied in the laboratory by examining cement and aggregate combinations with a scanning electron probe microanalyser. Pieces of opal and quartz were embedded in a medium alkali portland cement (0.71 Na_2O equivalent) with a 0.25 water/cement ratio, cured at 50°C. These specimens were then sectioned and polished in order to investigate the movement of ions at the aggregate/cement interface after a 24 hour storage period. Movement of ions is easily demonstrated with known alkali-silica reactive aggregate materials[3] but has not been reported in unreactive materials such as quartz. The effects of alkali-silica reaction with these specimens are illustrated in the series of photomicrographs in figure 1. These show the distribution of Na, Si, and Ca near the opal and quartz interfaces with the cement.

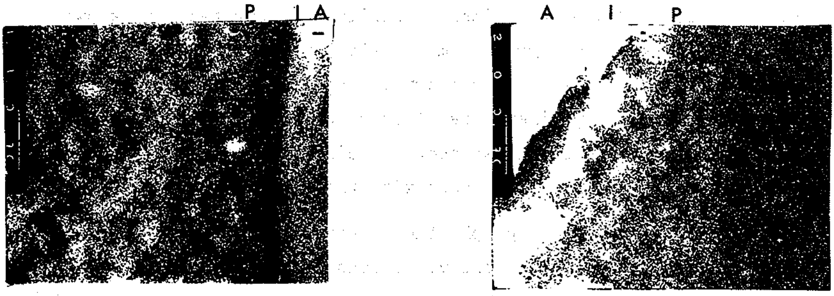
In these photomicrographs the sensitivity of the instrument has been varied in order to show the variations in concentration of each element and therefore although each photomicrograph gives a visual indication of the elemental concentration over each sample, the relationships between the photographs can only be considered in relative terms.

Scanning electron micrographs for iron show the expected random scatter with small local concentrations indicating the positions of ferrite phases. In figures 1 and 2 photographs I and II show local concentrations of sodium, which appears as a broad band in the cement paste about 100 microns from the interface with the opal. Photographs VII and VIII show the sodium and silica distributions for opal, but after storage for 240 hours at 50°C. Photographs III and IV are of the silica distribution and show an apparent infiltration of silicon into the cement possibly as a mobile gel produced during the 50°C curing process. The distribution of calcium is shown in photographs V and VI. These provide some evidence to show that calcium migrates into the reactive opal



I II

Sodium distribution at a Quartz(I),and opal interface(II) 50C,24 Hours.



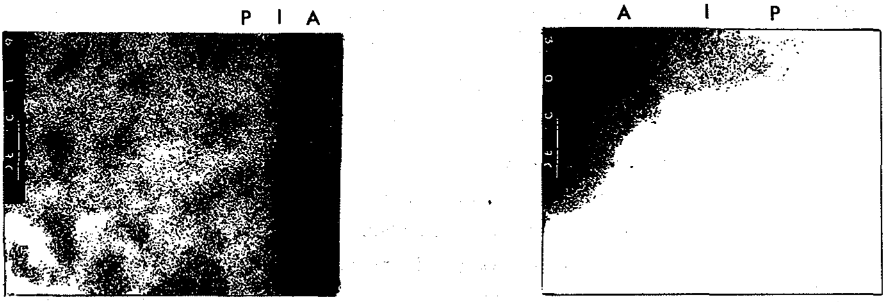
III IV

Silicon distribution at a Quartz(III),and Opal interface(IV) 50C,24 HOurs.

P:Paste **A**:Aggregate **I**:Interface

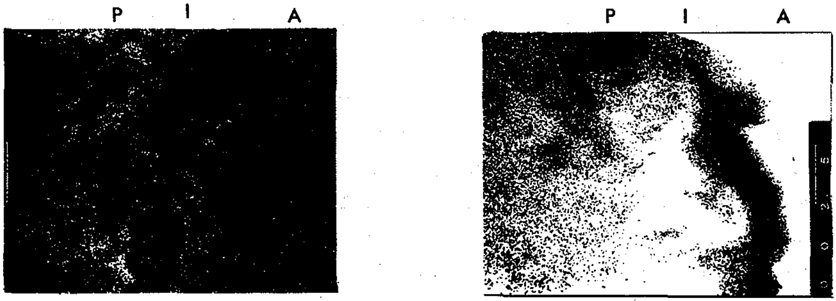
Elemental distributions at cement/aggregate interfaces.

Fig 1



V VI

Calcium distribution at a Quartz(V)and Opal interface(VI), 50C,24 Hours.



VII VIII

Sodium(VII) and Silicon(VIII) distributions across an opal interface 50C,240 Hours.

Elemental distributions at cement/aggregate interfaces.

Fig 2

with a decrease in concentration in the paste adjacent to the interface. This effect may be due to the rapid reaction of $Ca(OH)_2$ with silica to produce calcium silicate hydrate gels which act as barriers to further calcium migration to the interface as has been suggested by Lea[1].

The apparent modifications to the cement and aggregate chemistry during these early hydration reactions near the interface might be expected to have an effect on the cement/aggregate bond strength. In order to investigate possible changes in tensile bond strength a series of experiments were devised to study the variation in bond strength with temperature of curing, and to follow the reactive process in terms of its effect on tensile bond strength.

25mm diameter discs of opal and quartz aggregate were mounted on metal holders with araldite. The bonding surface of the disc was polished and freshly prepared cement paste with its holder cast directly onto this surface. Each specimen was moist cured for 2 hours and then stored under water at various controlled temperatures. At appropriate intervals the specimens were removed from storage and tested to failure totally immersed in water in a special jig.

The first series of test results were obtained using Brazilian rock crystal quartz and a pure low cristobolite opal and a medium alkali cement (0.71 Na_2O) with a slightly higher K_2O than Na_2O content. These results are reproduced in Figure 3. The lower 3 lines which are for opaline interfaces show that at first the bond strength increases rapidly, but before 20 hours at both 50°C and 75°C the curves level out because of the formation of an alkali-silica gel reaction product at the interface. At 30°C this effect takes 25 hours. Further increases in bond strength at 30°C and 50°C are cancelled out by the hygroscopic nature of the gel itself which after 48 hours can exert enough pressure to begin forcing the aggregate away from the cement. Strength then decreases until at approximately 66 hours the gel becomes fluid enough to ooze out of the specimen when bond strength begins to build up again. The subsequent increase in strength is probably due to a localised build up of further gel only at the more reactive sites on the interface while over the rest of the surface of the aggregate the cement is still in good bond contact. The results for curing at 75°C would appear to support this since no recovery is observed indicating that the whole area of the interface is reactive at this temperature.

Comparison of these three sets of results with those obtained with quartz shows that the effect of having a reactive aggregate becomes apparent at about 15 hours. The strength curves for quartz at 30°C and 50°C differ in that the higher curing temperature gives a lower overall strength after 15 hours. This effect may be explained by the observations of Neville[4] concerning compressive strengths of concretes cured at various temperatures. These results suggested that the rapid hydration at high temperature tends to produce a more porous concrete with incipient flaws which will give rise to early low tensile strengths.

The results indicated in the graph figure 4 were produced using a high alkali cement with a 1.10 Na_2O equivalent and similar K_2O, Na_2O contents. Comparison of the results for opal in figures 3 and 4 clearly show the effect of high alkalies in the cement, and the increased temperature effects produced with such a cement. These effects are most probably the result of increased alkali reactivity resulting from the higher alkali contents.

Conclusions

It is clear from these results that alkali-silica reactivity has a major effect on cement/aggregate bonding. Kennedy and Mather[5] have commented on the beneficial effect of mild alkali-silica reactions in 1953 improving bond strength for cherts from Treat Island, Maine. The work 1965 of Alexander, Wardlow and Gilbert[2] on the contact zone between cement and "inert" aggregates has shown that microhardness results are lower in the cement at the interface than elsewhere.

The results of this present investigation clearly show tensile bond strengths for both opal and quartz to be similar in the early stages of the curing of a concrete after which the strength of the reactive aggregate bond falls off, while that for quartz only levels off. The photomicrographs taken at an early stage in the curing of the experimental specimens show an increase in alkalies near the interface and this increase according to Alexander and Davis[7], McCoy and Eshenour[8], 1968 Alexander[9] should reduce paste strength. 1960

1959

The anomaly of an increase in strength at the interface, combined with a reported decrease in microhardness in the adjacent paste is a difficult one to resolve. Presumably it must be a matter of degree of operation of both processes. If reaction is very mild then the strength increase due to reactivity may supercede the effect of increased concentration of alkalies in the paste at the interface. If however, reaction is more pronounced, but at a time before any gel stages are reached, the paste failure will override any increase in bond strength at the interface.

The graphs in this paper may indicate this in that the high alkali cement has produced a concentration of alkali in the paste such that although surface bonding of the aggregate to the paste may be excellent, lack of intergranular adhesion in the contact zone produces an early failure.

The graphs, figures 3 and 4 seem to indicate that tensile bond strengths are temperature dependent although Alexander, Wardlow and Gilbert[6] suggested that bond strength may be independent of temperature under certain conditions. In the light of these experiments perhaps this should be modified in that bond strength is independent of curing temperature providing the aggregate shows no surface chemical reactivity with cement paste.

Acknowledgements

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increase in
[illegible] of interface

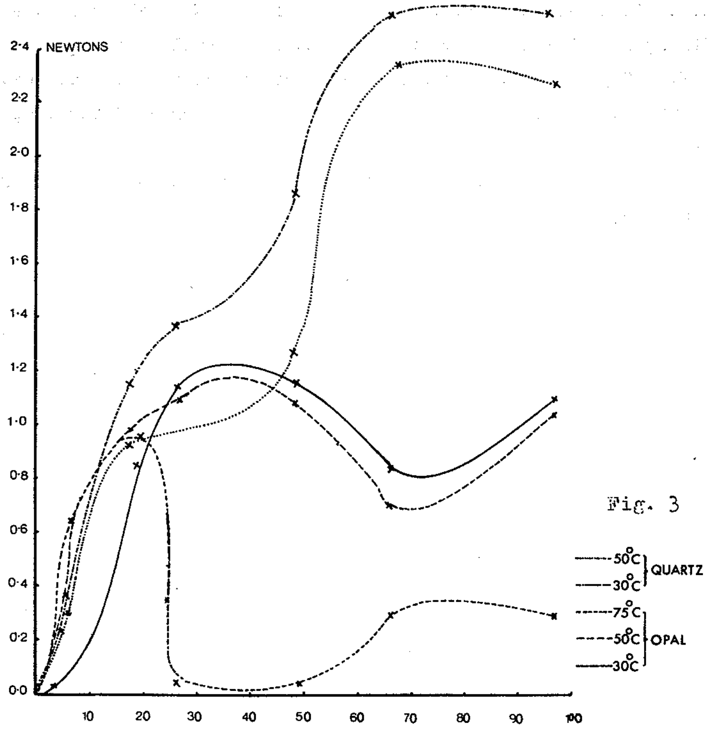
aggreg.

L opal
tensile strength similar
early stage;
levels off fallsoff
later stage

paste

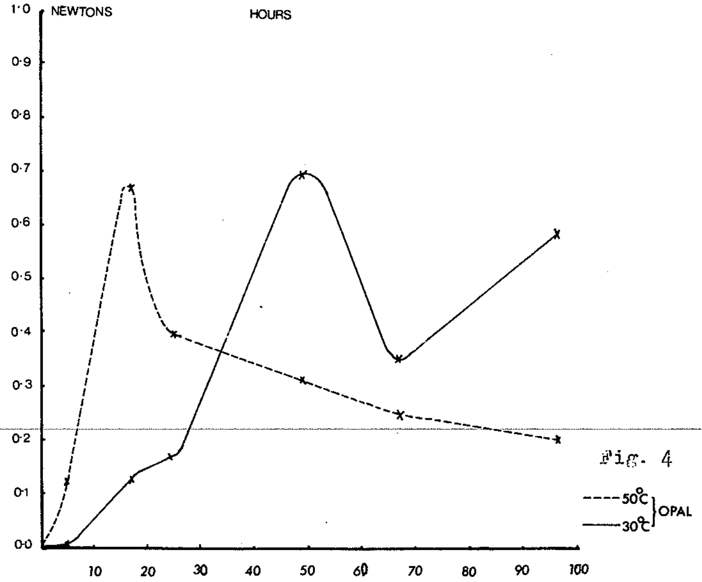
microhardness lower strength

reaction mild very
strength due to reactivity supersedes
the effect of concentration of alk.
reaction pronounced
before gel stages paste failure
high alkali
concentration of alkali → good bond
but intergranular adhesion in contact
zone poor
tensile bond → dependent on t°
of alkali reactive material
strength independent on t°
of alkali reaction strength dependence



2·4 NEWTONS
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0·0
10
20
30
40
50
60
70
80
90
100
50°C QUARTZ
30°C QUARTZ
75°C OPAL
50°C OPAL
30°C OPAL

Fig. 3



1·0 NEWTONS
HOURS
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
10
20
30
40
50
60
70
80
90
100
50°C OPAL
30°C OPAL

Fig. 4

INFLUENCE OF ALKALIES ON THE HYDRATION OF CEMENT

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Abstract

The setting of cement is closely related to the compositon of mixing water solution. Rapidly dissolved alkalies, especially the alkali sulfates of the clinker, increase the pH-value and lower the calcium hydroxide concentration of the solution. This fact seems to increase the hydration velocity of the C_3A, particularly during the first minutes of hydration, before the dormant period stops further reactions. C_3A-rich cements with a lack of gypsum show rapid setting caused by formation of aluminate hydrates. With gypsum in excess rapid setting by formation of large amounts of ettringite may occur. The increase of the temperature in fresh concrete mixes has a similar effect on setting as an increase of OH^--concentration caused by alkalies diluted from the cements. Rapid setting can be avoided by exact balancing of calcium sulfate contents by different provisions in ① the plant and by decreasing ② the temperature of fresh concrete.

alk↑

Ca↓

↑Hydra

OH conc

= ↑ t°

1. Introduction

Consistency and workability of concrete depend on its composition. They are essentially influenced by the properties of the cement used, the cement content and the grading of aggregate. Additives used, time of mixing and temperature of fresh concrete as well as the time during which concrete is transported from the mixing plant to the building site and the continuous mechanical motions of the concrete during the transit may also be of practical importance.

In order to find out whether these factors are of major influence on practical application of cement, extensive studies have been carried out at the "Forschungsinstitut der Zementindustrie" since a longer time. The investigations at first were mainly focused on the effects of cement composition and manufacturing conditions on the setting of cement[1,2,3]. More recent studies are concerned with the effects of additives, temperature of fresh concrete and mechanical motions on the consistency of concrete. Further objectives of research are to examine whether the composition of the mixing water solution may effect the setting of cement.

2. Present state of investigations

The setting behaviour of the cement influences mainly the workability of the concrete and for this reason certain requirements have been standardized in the cement-producing countries. Chemical reactions between the cement constituents and the mixing water decisively influence the setting behaviour. The reaction products developing thereby bridge the water-filled space between the cement particles and by this build up a structure which gradually grows stronger with time. This formation of a structure lowers the consistency of cement paste, mortar or concrete.

In the first reactions which take place immediately after the addition of the mixing water nearly exclusively the tricalcium aluminate of the cement clinker and the calcium sulfate added to regulate the setting participate. Normally the reaction product formed is ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$). In the case of insufficient calcium sulfate monosulfate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$) and tetracalcium aluminate hydrate ($4CaO \cdot Al_2O_3 \cdot xH_2O$) are developed. Additionally, the alkali sulfate content of cement clinker, the alkalies in the hydrated portion of the C_3A and calcium hydroxide, formed by hydration of the free CaO or by an initial surface reaction of the calcium silicates are dissolved. The initial reactions which in most cases only last a few minutes are followed by a dormant period of 2 to 6 hours.

According to the older literature on this subject[4,5,6,7] the dormant period as well as set retardation were explained to result from the effect of gypsum. The interruption of the hydration reactions shall be caused by an ettringite cover on the surface of the aluminates. The reactions would start again as soon as the gypsum in solution has been consumed.

More recent investigations[3], however, have shown that the dormant period is not based on the effect of gypsum. The dormant period occurs with gypsum containing cements as well as with sulfate-free clinkers. The examinations also showed that the setting of cement already starts during the dormant period. In the presence of sufficiently high amounts of calcium sulfate 3 to 6 % by weight of ettringite normally are formed from the C_3A which reacted at the beginning of the hydration within the first minutes. The ettringite appears on the surface of the cement particles mostly in the form of fine crystals, smaller than 1 µm.Electron microscopic investigations showed that later on the ettringite grows by recrystallization or coarsening crystallization and that the ettringite crystals consequently begin to bridge the pore space. The recrystallization and the formation of a structure during the dormant period leads to the setting of the cement.

The investigations have indicated so far that the course of setting of a cement is determined by the type and the amount of hydration products which are formed during the first 5 minutes. Decisive for this are the influencing factors given in table 1.

Fig. 1: Influences on the setting of cement

1. COMPOSITION OF CEMENT		2. MANUFACTURING OF CEMENT
C_3A CONTENT		COOLING RATE OF CLINKER
TOTAL ALKALI CONTENT		STORAGE OF CLINKER
ALKALI SULFATE CONTENT		CEMENT TEMPERATURE DURING GRINDING
TOTAL SULFATE CONTENT		WATER INJECTION INTO MILL
CALCIUM SULFATES:	$CaSO_4 \cdot 2H_2O$	FINENESS OF CEMENT
	$CaSO_4 \cdot 1/2H_2O$	STORAGE
	$CaSO_4$	
ADDITIVES		

Above all the amount and the reactivity of the C_3A and of the various calcium sulfates is of importance. The reactivity is mainly induced by the cement composition and the conditions during the production of the cement, such as for instance the velocity of clinker cooling, the temperature and the relative humidity during grinding and storage of the cement.

The reactivity of the clinker with the mixing water also determines the composition of the solution, that is how much alkalies, calcium hydroxide and sulfate the solution contains and which pH-value emerges. The literature gives differing data 8,9) on this subject. But these data allow no conclusions on the reason for the appearing differences. The composition of the solution is not only significant for the setting, but also for the development of strength 10), the alkali-aggregate reaction 11,12) and the reaction of pozzolans.

3. Cements

To examine the influence of the composition of the solution on the setting of the cement, several cements have been selected which differed in their contents of tricalcium aluminate, alkalies and calcium sulfate as gypsum ($CaSO_4 \cdot 2H_2O$) or semi-hydrate ($CaSO_4 \cdot 1/2H_2O$). In figure 2 the most important properties of the used cements are presented. Some of the cements were mixed from plant-made clinkers with calcium sulfates and others have been plant-made cements. The C_3A content calculated according to Bogue ranged from 10.9 to 13.4 % by weight and the total alkali content from 0.06 to 1.60 % by weight Na_2O-equivalent. The amount of alkalies in the clinker bound as sulfate ranged from 6 to 100 %. The laboratory mixed cements contained 1.5 to 5.0 % by weight of sulfate as gypsum or as semi-hydrate.

Fig. 2: Composition of cements

	C_3A (BOGUE) [W-%]	$\sum NA_2O+0{,}658\ K_2O$ [W-%]	DEGREE OF SULFATISATION [%]	TOTAL SULFATE IN CEMENT [W-%]	SPEC. SURFACE [CM^2/G] BLAINE
LABORATORY MIXED CEMENTS FROM CLINKER					
AW	11,2	0,06	75		4 000
DM 100	13,4	0,83	100	1,5 - 5,0	± 100
WO 2	11,9	0,94	6		
TECHNICAL CEMENTS					
PZ AG/68	12,0	0,80	31	2,6	APPR.
PZ LA/68	12,8	1,60	45	3,1	3000 - 3500
PZ B/350	12,9	0,31	14	3,4	
PZ S/350	10,9	1,02	61	2,8	

4. Test results

4.1 Setting of cement

The change in the consistency of the laboratory-mixed cements of clinker "AW" and "DM 100", which is related to the setting, was measured with a penetrometer. The amount of the appearing ettringite, syngenite and secondary gypsum was determined with a DSC-calorimeter (Differential-Scanning Calorimeter) after 1 hour of hydration. The results of some of these investigations are illustrated in fig. 3 and 4. In the diagrams on the left the course of setting and on the right the new formed phases have been plotted versus the total sulfate content of the cements.
The sulfate was added to the cements as gypsum (continuous line) or as semi-hydrate (dashed line).

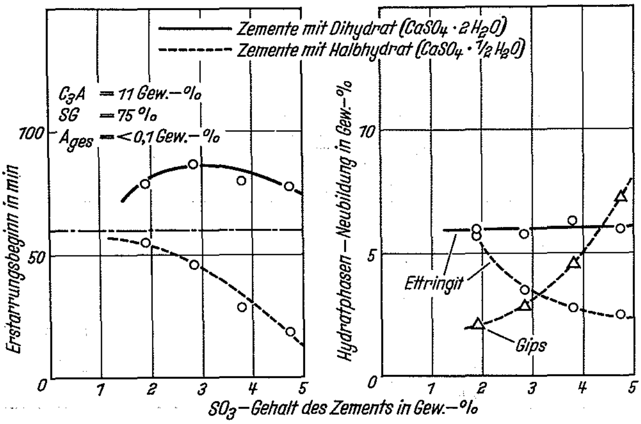

Fig. 3: Cements made from clinker "AW" - Setting and formation of hydrated phases.

In fig. 3 the results from cements "AW" which were rich in C_3A and poor in alkali are presented. Summarized the result is that the gypsum-containing cements set approximately after more than 70 minutes. With 3 % by weight of SO_3 the setting time shows a flat maximum. During the first hydration which takes place before the dormant period begins, a nearly constant amount of approximately 6 % by weight of ettringite independent of the amount of added sulfate was formed. Aluminate hydrates have not been estimated. If the cements contain semi-hydrate instead of gypsum how it may occur in the mill with grinding temperatures exceeding 80 °C or after a prolonged silo storage, gypsum is precipitated from the solution and rapid setting takes place. Because of the formation of this secondary gypsum the quantity of ettringite decreases.

Fig. 4 demonstrates the setting of cements made from clinker "DM 100". They mainly differ from the cements "AW" in a higher C_3A-content of 13 % by weight and a medium-high total alkali content of 0.8 % by weight Na_2O-equivalent. Similar to the cements "AW" the C_3A of the cements "DM 100" does not contain alkalies. Whereas the cements "AW" had a low total content, the alkalies of cements "DM 100" are completely bound as sulfate.

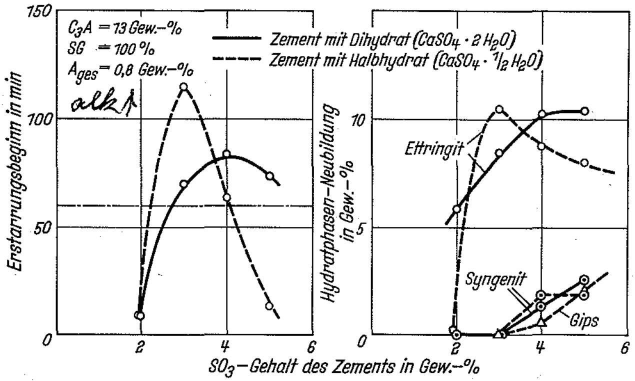

Fig. 4: Cements made from clinker "DM" - Setting and formation of hydrated phases

The gypsum-containing cements "DM 100" show a sharper maximum in the setting time at approximately 4 % by weight of SO_3. Cements poorer in gypsum content set more rapidly, since more aluminate hydrate and monosulfate are formed which build up a bridgeing structure. With a higher content of gypsum the cements change their consistency because of a formation of more than 10 % by weight of ettringite. "DM 100"-cements with semi-hydrate set in a similar way. But with high sulfate contents the excessive formation of ettringite is accompanied by a precipitation of secondary gypsum which together lead to rapid setting. Rapid setting caused by ettringite is especially favoured by such cements in which the C_3A has a still higher reactivity because of large amounts of alkalies in solid solution. Such a behaviour would show for example cements of the type "WO 2" according to fig. 1.

With the exception of the alkali content the cements "AW" and "DM 100" differ only slightly and yet both cements set in different ways. However, since the alkalies in the cements "DM 100" are exclusively present as alkali sulfate, it may be expected that they will go into solution and thereby affect their composition immediately after addition of the mixing water.

4.2 Composition of the solution

The composition of the solution was determined after 1 h of hydration, that is during the dormant period of the cement. On the left of fig. 5 the obtained alkali contents and on the right the determined calcium oxide contents of the solution have been plotted. The measurements led to high alkali contents of 50 to 60 mmol/l in the solution of the cements "DM 100", whereas with the low-alkali cements "AW" virtually alkali-free solutions have been found.

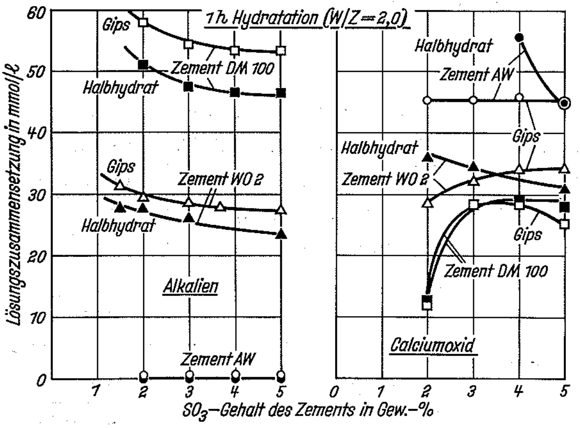

Fig. 5: Composition of the solution after 1 h of hydration

On the other hand the solution of the low-alkali cements "AW" contained fairly large amounts of calcium oxide, whereas the solution of the alkali-rich cements "DM 100" showed a alltogether lower CaO-content, which increased with added calcium sulfate. The measurements did not show in the single case whether calcium hydroxide or calcium sulfate were dissolved. But according to the fact, that the pH-value of the high-alkali solutions was higher than that of low-alkali but Ca-rich solutions, the conclusion may be drawn that higher OH$^-$- or alkali hydroxide contents in solution lead to correspondingly lower amounts of calcium dissolved as calcium hydroxide according to the solution equilibrium of N. Fratini[13)]. The remaining calcium seems therefore to be dissolved as calcium sulfate, whose solubility - according to literature[14)] - is said to be increased in solutions rich in alkali hydroxide.

Former investigations of the equilibrium in pure solutions of calcium hydroxide and alkali hydroxide[15,16,17)] led to similar conclusions. The result of recent investigations in which alkali sulfates were added to alkali and calcium hydroxide containing solutions is shown in fig. 6.

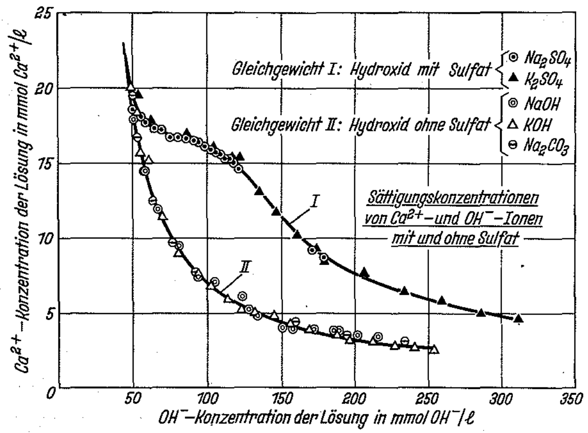

Fig. 6: Concentration of Ca^{2+}- and OH^--Ions in saturated solutions with and without sulfate.

Curve II demonstrates that according to the mass action law the solubility of calcium hydroxide decreases with increasing OH^--concentration added as NaOH or KOH. In the presence of sulfate (curve I), however, the Ca^{2+}-concentration of the solution decreases slower at higher OH^--concentrations. The added alkali sulfate seems to react with the calcium hydroxide whereby alkali hydroxide besides gypsum and syngenite are formed. According to

DSC-analysis of the solid phase the gypsum remains in solution almost completely, apparently favoured by alkali hydroxide up to concentrations of approximately 100 mmol/l. From this result may be concluded that an increased calcium solubility in alkali and sulfate containing solutions is due to an increased gypsum solubility but not so much to a supersaturation of calcium hydroxide.

This result is of interest for the hydration of cement. In general the sulfate is almost completely consumed after 1 d by reaction with C_3A to ettringite and in that case the pore solution of a hardened cement paste is mainly influenced by the alkali and the calcium hydroxide content according to the equilibrium of curve II in fig. 6. The equilibrium between alkalies, calcium and sulfate may therefore be of importance only in the earliest stage of hydration in wich the cement sets. This is suggested by tests performed with 3 plant made cements. The changes in the composition of the liquid phase were determined in relation to the time of hydration.

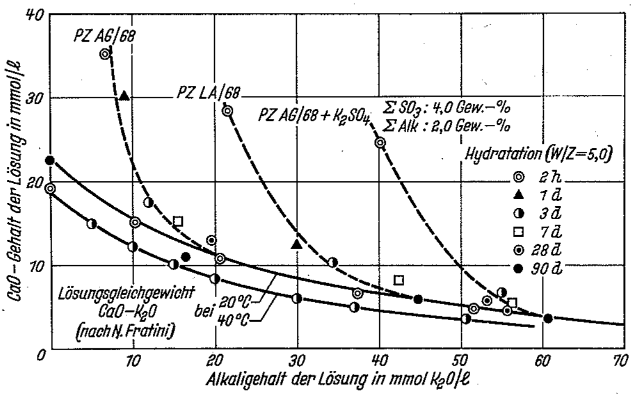

Fig. 7: Influence of time and temperature on the equilibrium between calcium and alkalies in the solution of cement pastes.

The results in fig. 7 demonstrate that all solutions contained after 2 hours of hydration large amounts of CaO which far exceed the CaO/K_2O-solution equilibrium. The high sulfate content found simultaneously in the same solution leads to the conclusion that the increased Ca^{2+}-solubility is mainly caused by gypsum. After subtracting the amount of CaO equalling the analyzed SO_3 content the measuring points almost exactly fall to the equilibrium curve. On the other hand the Ca^{2+}-solubility was reduced by prolonged hydration and the measuring points were the more approached to the equilibrium curve as the sulfate of the solution was consumed by reaction with the aluminate of the clinker. With prolonged hydration the points furthermore shift to higher alkali contents. That is due to the fact that with advancing hydration mainly of the C_3A still more alkalies are liberated, shifting the equilibrium of the solution correspondingly. Finally, the diagramm shows as a result of the literature13) that the solubility of calcium hydroxide is reduced by rising temperatures too.

5. Conclusions

The obtained results lead to the following conclusions: Evidently the time during which a cement sets is closely related to the composition of the mixing water solution. This has been exemplified by the different behaviour of 2 cements which differed only in their content of alkali sulfate. Although both clinkers contained the relatively inactive cubic aluminate, more C_3A, however, reacted during the first minutes in the presence of higher alkali contents and with higher pH-values in the solution. If there was a lack of gypsum, mainly aluminate hydrate was formed resulting in rapid (a) setting. With a too big supply of sulfate excessively large amounts of ettringite developed also leading to rapid setting. (a) It seems to be that with higher amounts of ettringite already a relatively small increase in the crystal size by coarsening crystallization is sufficient to bridge the water-filled pore space and thereby build up a structure.

Higher amounts of alkalies in the clinker, particularly of alkali sulfates, which are rapidly dissolved, lower the calcium hydroxide concentration of the solution, thereby increasing the hydration velocity of the C_3A prior to the dormant period. The possibility of rapid setting therefore always exists, if such cements are not perfectly balanced in their sulfate content. Similar results were found by P.K.Metha[18,19], when he investigated the properties of high early strength cements. In that case, however, the accelerating effect of alkalies is desirable. It has been pointed out by W. Lieber[20] too that the reaction of the C_3A can be speeded up substantially with high OH^--concentrations in the mixing water solution. These results lead to the conclusion that the operation characteristics of additives and their application in concrete technology could by this way more effectively be tested.

According to these investigations an increase in temperature of the fresh concrete has much the same effect as an increase in OH^--concentration caused by alkalies.

In view of the workability of concrete it can be deduced from the results that it is above all important to retard the hydration of the C_3A sufficiently within the first 5 minutes. This can be done in normal cases, for instance, by well regulated cement properties, by decreasing the temperatures of fresh concrete and by reduced motions in transit.

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THE EFFECT OF ADMIXTURES ON ALKALI-AGGREGATE REACTION IN CONCRETE

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Abstract

With expansion measurements on concrete containing opal as alkali-reactive aggregate the efficiency of admixtures was tested. Several fly ashes, trass, ground cristobalite and a SiO_2-glass dust were used as admixtures. The specific surfacec of the substances ranged from 2800 to 24000 cm^2/g.

The tests showed that the efficiency of admixtures can only be judged if not part of the cement, but a part of the fine sized aggregate in the concrete is replaced. For this judgement the specific surface is important too. Alkali expansion in concrete can be prevented completely by suitable dust-fine admixtures. The efficiency of admixtures is due to the chemical reactivity with alkalis in the pore solution and possibly also to an increased pore volume in the concrete. Glasses with medium SiO_2-contents seem to be more suitable than glasses or crystalline substances with SiO_2 contents of more than 95 % by weight. The use of admixtures is limited by requirements for the concrete quality, such as strength, watertightness and freeze/thaw resistance.

1. Introduction

Former investigations have shown that the course and the extent of the alkali-aggregate reactions in concrete are dependent on the alkali reactivity, the quantity and the grain size distribution of the aggregate, the alkali content of the cement, the cement content and the environmental conditions 1,2,3). The knowledge from these extensive tests served as a basis for working out a recommendation with special attention to the conditions in North Germany. In this recommendation precautionary measures against a deleterious alkali-aggregate reaction have been laid down4).

The precautionary measures are primarily based on an examination of the alkali reactivity of the used aggregate. Practical experience has shown that it is only the content of opaline sandstone and of reactive flint which is decisive and which is~~t~~ therefore determined with established testing procedures5). As a further precautionary measure the use of cements with low effective alkali content (NA-cement) has been introduced. These cements are required only for cases in which the aggregate has a certain amount of reactive constituents and the concrete additionally is exposed to disadvantageous environmental conditions. Such environmental conditions are for instance the permanent wetting of a construction and an alkali supply from outside, for instance by seawater or de-icing salts.

Further precautionary measures, which have not been incorporated in the recommendations, are the reduction in the cement content, if possible, according to the quality of the concrete. In some cases a better aggregate grading can also be of benefit. Also the addition of a more or less large amount of natural or artificial pozzolans to the concrete is often regarded as an effective measure to avoid a deleterious alkali-aggregate reaction. In order to examine the effectivity of such pozzolans it is necessary to distinguish whether a part of the cement or a part of the aggregate shall be replaced.

Admixtures which are thought to prevent deleterious alkali expansion are for instance fine-ground silica, opaline rock, volcanic glasses, diatomeen earth, trass, calcined clay and also fly ashes6,7). It is assumed that this effect is chiefly due to the chemial reactivity of the silica in such admixtures with the alkali hydroxide in the pore solution. If that is true, a shift of the pessimum of the reactive aggregates originally present should occur. Experiments with opal as a reactive admixture showed that it is in particular the opal quantity substituted in the quartz grain sizes < 0.2 mm that can prevent alkali expansion 8,9), if the sum of the opal quantity originally present and the opal quantity added is larger than the pessimum concentration of the reactive aggregate. It seems that besides opaline rocks no other admixtures have been tested in this way.

The majority of the experiments to test the effect of admixtures followed ASTM C 441. In that case not the aggregate, but a portion of 5 to 40 % by weight of the cement is replaced. Very often the water-cement ratio too had to be increased in order to maintain the workability of the concrete. With such a test procedure the found reduction in the expansion of specimens might be either the result of a pozzolanic reaction of the admixtures or the result of a dilution of the cement quantity. According to former investigations 3) such a reduction of the cement content is associated with a decrease in the effective alkali or OH^--content in concrete. This alone would therefore already lead to a drastic reduction in the alkali expansion.

From test results so far known it can be assumed that the various substances recommended as admixtures apparently show different chemical reactivity. Decisive might be in which form the reactive proportion of the silica is present and which grain size or surface the admixture has 6,7). Occasionally it is also recommended to improve the effect of natural or artificial pozzolans by finer grinding 10) or by remelting with the addition of lime 11).

The effect of various admixtures could be examined more reliable, if they were tested under the same conditions. This means that the cement content and thus the effective alkali content in the concrete have to be kept unchanged. For these tests a part of the aggregate and not a part of the cement should therefore be replaced by the admixtures.

In addition to the chemical reactivity of the admixture the physical properties of the hardened cement paste, of the aggregate and of the concrete may also influence alkali expansion. It has already been stated that a deleterious alkali-aggregate reaction not only requires a high reactivity of the aggregate constituents, but also a low porosity [1]. This in particular applies to opal and various glasses which in normal case have no marked porosity. Experiments on flints with densities of < 2.53 to > 2.59 g/cm^3, on the other hand, showed with an approximately equal reactivity alkali expansion decreases as soon as the porosity rises. Similar to the effect of the porosity of the aggregate could be that of the capillary porosity of the hardened cement paste, leading with increasing water-cement ratios of the concrete to a reduction in the expansion. For this reason some additional tests have been performed to learn more about the influence of the capillary porosity.

2. Tests

In accordance with ASTM C 441 concrete specimen 2.5 x 2.5 x 28.5 cm were produced. The concretes contained approximately 600 kg cement per m^3 with a constant water-cement ratio of 0.45[1]. It was only in a further test series that larger amounts of water were added to the concretes to increase the capillary pore volume in the hardened cement paste. The water-cement ratios were thereby increased to 0.60. The aggregate consisted of 6 fractions with a maximum grain size of 15 to 16 mm. As a reactive aggregate constituent pure opal in the grain size < 0.09 mm was chosen and added to the concrete in a quantity of 4 % by weight, based on the aggregate. This quantity was equal to the pessimum concentration for opal in that fraction. The specimens are stored at 40 °C and more than 95 % relative humidity. The results obtained so far are related to a storage time of 2 months.

#16

Up to 20 % by weight of the aggregates were replaced by the admixtures trass, fly ash, cristobalite and an amorphous-glassy silica product (SiO$_2$-glass dust) mainly in the size fraction < 0.2 mm. The concretes containing admixtures were tested with and without opal.

	DENSITY [G/CM^3]	SPECIFIC SURFACE [CM^2/G]
QUARTZ	2,65	-
OPAL	2,06	-
CRISTOBALITE	2,35	3 500
SIO$_2$-GLASS	2,21	24 000
TRASS	2,42 - 2,48	5 800 - 6 300
FLY ASH	2,20 - 2,44	2 800 - 3 300

Fig. 1: Density and specific surface of used additives and aggregates

The table presented in fig. 1 shows that the trass had a specific surface according to Blaine of approximately 6000 cm^2/g. The surface of the fly ashes and of the cristobalite dust ranged from 2800 to 3200 cm^2/g. With approximately 24000 cm^2/g the SiO$_2$-glass dust showed the greatest fineness. The measured densities of the admixtures were in the range of 2.20 to 2.48 g/cm^3.

3. Test results

3.1 Porosity of the hardened cement paste

The experiments were carried out on concretes with an unchanged cement content of approximately 600 kg per m^3 and with 4 % by weight of opal, based on the aggregate. The fresh concrete mixes contained different quantities of water with a water-cement ratio ranging from 0.40 to 0.60.

The capillary porosity of the hardened cement paste in relation to the water-cement ratio was calculated by a method described by F.W. Locher[12)]. For this purpose a hydration degree of the cement of 1 was presumed. Taking into account the chemical shrinkage, capillary pores are formed in a concrete with a water-cement ratio of more than 0.36, which increase the total porosity of the concrete. In fig. 2 the expansion of the concrete specimen was plotted versus the calculated volume of the capillary pores of the hardened paste.

It shows that with water-cement ratios exceeding 0.48 and a capillary porosity of 15 % by volume respectively the expansion due to alkali expansion falls linearly. The decrease is approximately 1 mm/m per 0.03 water-cement units. With lower water-cement ratio respectively pore volume the influence diminishes due to perhaps still uncomplete hydration of the cement and an uncomplete compaction of the concrete specimen.

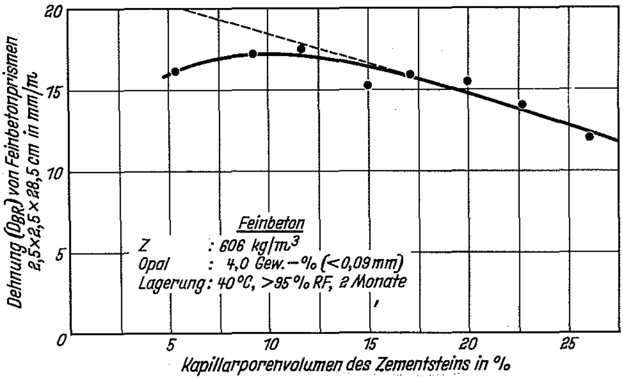

Fig. 2: Influence of the capillary pore volume of the hardened cement paste on the expansion of opal containing concrete specimen.

Further experiments have still to be carried out to investigate the physical properties of the prisms. But already now it can be concluded that the porosity of the hardened cement paste and of the concrete might help to reduce measurably the expansion caused by alkali aggregate reaction. The reaction product formed seems to be able to penetrate partly into the open pore spaces of the concrete and of the hardened cement paste. Therefore a comparison of the chemical efficiency of admixtures or a test of other influencing factors is only possible if besides the concrete composition the water-cement ratio also remains unchanged.

As a precaution against alkali expansion an increase in the capillary porosity is not suitable, since it reduces the concrete strenght and furthermore lowers the diffusion resistance to the ions penetrating from outside[13].

3.2 Chemical reactivity of admixtures

The expansion of a concrete which contained besides quartz sand and gravel 4 % by weight of opal was taken as basis for calculating the percentage of length change in all the other concretes. After 2 months the measured expansion of that reference concrete averaged 17.5 mm/m. The expansion of all other concretes which contained graduated amounts of admixtures besides 4 % by weight of opal are presented in fig. 3.

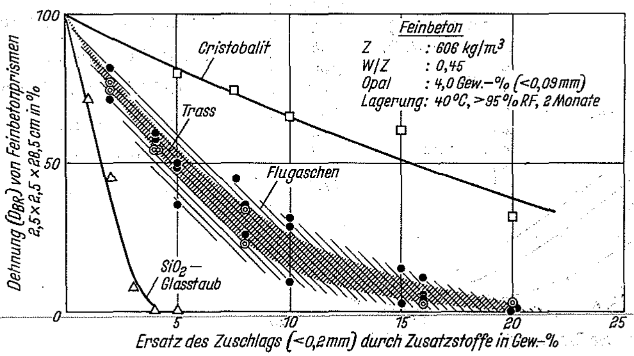

Fig. 3: Decrease of expansion by several kinds of admixtures independent on their specific surface area (Blaine). The quantity of admixtures is based on the total amount of aggregate.

It can be seen that all admixtures which were used instead of quartz sand diminish the expansion of opal-containing concrete. In concretes which with respect to workability contained 20 % by weight of cristobalite at the most, expansion was only reduced to approximately 30 %. It seems that in this kind of presentation the SiO_2-glass dust was the most effective admixture, because an addition of 4 to 5 % by weight at the most was sufficient to prevent the expansion entirely. A medium position with a reduction of expansion to a range of 60 to 35 % was taken by fly ashes (wide hatching) and trass (narrow hatching).

However, this presentation does not give any information about the grade of reactivity of the various admixtures since there is no uniform comparative basis. Owing to their different surface areas the substances were added in different quantities to the concrete. This was necessary in order to achieve a consistency which still allowed complete compaction of the concrete. To study the influence of quantity and surface of the admixtures together, the specific surface of the admixtures was multiplied with the quantity of the substance in 1 m^3 concrete.

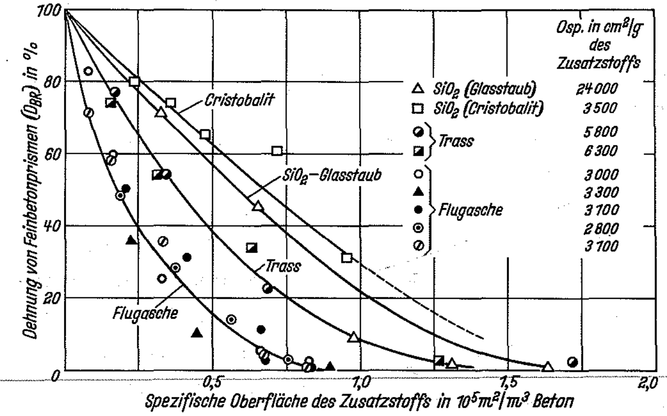

Fig. 4: Decrease of expansion by several kinds of admixtures according to their specific surface area (Blaine) and quantity in concrete.

In fig. 4 the percentage expansion of the concrete prisms has been plotted versus the total specific surface of the admixture per m^3 concrete. This again shows that the expansion decreases with rising surface proportions of the admixture. But on the basis of an equally large surface proportion of for instance $0.5 \cdot 10^5$ m^2 per m^3 of concrete it is found that fly ash glasses seem to be more reactive than trass, than cristobalite and the almost pure SiO_2-glass dust. On the basis of that evaluation also the differences between the 5 fly ashes became smaller. This is apparently due to the fact that the ashes of pit-coals from the Ruhr-Carbon have roughly the same composition and that they have been formed under similar conditions. The influence of their different alkali content is still to be tested.

The test results allow the conclusion that all admixtures react chemically with the pore solution in the concrete thus binding alkalies. At equal surface areas their efficiency is manifested in a more or less pronounced reduction of the concrete expansion caused by opal. But the admixtures tested are evidently more inactive than opal. Depending on their surface, admixture contents of up to 15 % by weight, based on the quantity of the aggregate, are necessary to reduce the expansion to values under 20 %. Using opal as an admixture this would only require an addition of a further 4 % by weight.

The alkalies bound by the admixtures apparently do not lead to a measurable expansion. This was proved by experiments on concrete specimen which contained the same graduated amounts of admixtures instead of quartz < 0.2 mm, but no opal. Although the used admixtures react with alkalies, they seem to have no measurable pessimum in this grain size. However, according to Australian[14)] investigations expansions can be measured as soon as the grain size of some of these admixtures exceed 0.2 mm.

The effect of fine ground admixtures with such a relatively small reactivity seems to be based on the formation of alkali silicates which have an alltogether higher molar SiO_2-content than the silicates formed by reaction between alkalies and opal in pessimum concentration. First experiments have already shown that SiO_2-rich alkali silicates swell considerably less with water than alkali-rich silicates. That means, that according to the chemical reactivity of the used admixtures the pessimum of the reactive opal aggregate will be shifted.

Besides the chemical effect of admixtures also a change in the physical properties of the concrete has to be taken into consideration. Many of the used admixtures contain a pore space of 1 (Trass) to nearly 20 % of volume (fly ash), which increases the pore space of the concrete and may possibly work as a reservoir for reaction products thus reducing an expansion.

4. Conclusions

The investigations lead to the conclusion that the efficiency of admixtures can only be judged under constant test conditions. For that reason not a part of the cement, but only a part of the aggregate in the size fraction < 0.2 mm should be replaced. The concrete composition should remain unchanged. Besides this the mass-related specific surface of the admixture should be taken into consideration.

The investigations have shown that the expansion of opal-containing aggregates in the concrete can be avoided by the use of suitable admixtures. Their efficiency is mainly due to the chemical reactivity, but possibly also to an increase in the total pore volume of the concrete. The pore volume may be increased as well by admixtures as in the case of higher water-cement ratios also by the capillary pores in the hardened cement paste.

The reactivity of glasses with SiO_2-contents of approximately 50 % by weight is apparently greater than that of the tested crystalline substances with a similarly high SiO_2 content or that of the glasses and crystalline substances with more than 95 % of SiO_2, if the real quantity of active surface area is taken into consideration. To reduce alkali expansion it is therefore necessary to overtake fineness and quantity of the admixture into the requirements of a concrete mix. However, requirements for the concrete qualtity, such as strenght, watertightness and freeze/thaw resistance, limit the use of admixtures. An increase in the water-cement ratio in order to raise the capillary porosity or to improve workability is therefore no advisable measure.

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4. INVESTIGATIONS OF THE REACTION MECHANISMS

WATER ABSORPTION AND VOLUME CHANGES OF ALKALI SILICATES IN FLINT MEASURED BY THERMOGRAVIMETRY

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ABSTRACT

Only the amorphous marked and micro-crystalline silica in aggregates causes alkali-silica reaction and expansion in concrete. One member of this group is flint. Using grains of flint which had been treated with alkali, it could be proved by means of thermogravimetry measurements at a temperature of 900°C that silica with lattice defects, such as flint, absorbs water differently. The absorption of water and the increase in volume of flint, is only possible in the presence of hydroxyl ions. Grains of flint stored in neutral NaCl/KCl solution did not show any increase in absorption. Contrary to this, flint stored in 1 normal NaOH/KOH solution showed a definite increase in the absorption of water.

Despite the numerous experiments with the alkali-silica reaction in concrete, one has not been able to give a full explanation for the expansion of the reactive aggregates. In this report we aim to prove that silica with lattice defects does infact absorb water and increase in volume, in the presence of alkali and hydroxyl ions. By the means of thermogravimetry we investigated the water sorption of flint as a representative of reactive silicas.

Bonded Water in Silicas and Flint

Depending on the nature and amount of the lattice defects, the silica minerals contain either more chemically bonded water (SiOH-groups) or molecular water. The most external or internal interfaces of reactive silica are covered with hydroxyl ions. More water can be added to the silanol groups due to further adsorption. Lange (2) described previously two sorts of molecular, adsorbed water in silicas:

SINGLE GROUP *DOUBLE GROUP*

FIG. 1

Hydoxyl groups at SiO_2-interfaces (1)

1. Physically adsorbed water with slight activation energy and
2. Water bonded at the SiOH-groups with a high activation energy.

When heating in a vacuum, first the SiOH double groups are decomposed in the formation of reversible oxygen links and SiOH single groups. Following this, there is a further decomposition of the SiOH single groups. At 400 °C the silica lattice is displaced.

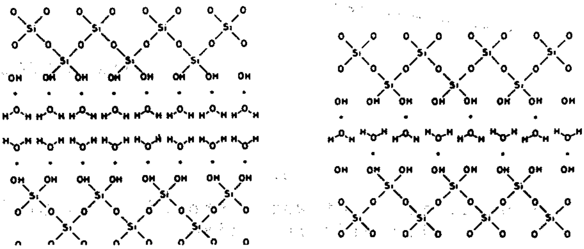

FIG. 2
Silanol groups and water layers at the quartzite interfaces in flint (3)

With respect to flint, Micheelsen (3) presumed that the interfaces of the quartzites, which build up the flint, are covered by single layers of SiOH-groups and that the neighbouring quartzites are bonded through several layers of water molecules. There are free SiOH-groups and oxygen links at the interfaces of quartzites in the ratio of 2:1. Overall, Micheelsen (3) found that the relationship between molecular water and the SiOH-groups in flint was 1:3.2.

The thermogravimetry measurements showed that the water in the fine flint grains is much more loosely bonded (see FIG. 3). The flint grains with the size of 0.05 - 0.07 mm release mainly the bonded water between a temperature of 400 °C and 600 °C. There are more external interfaces with slighter

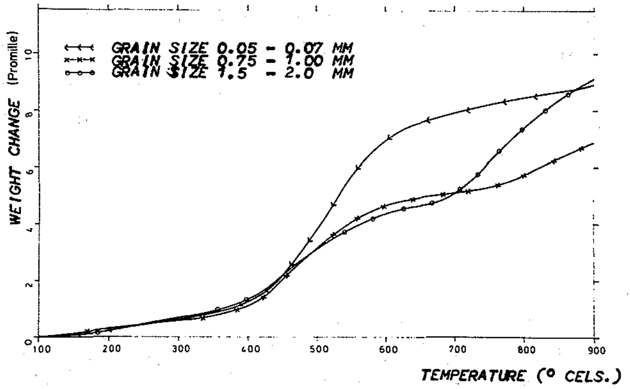

FIG. 3

Thermogravimetry of water stored flint grains with different sizes

activation energies in the fine flint grains.

Water Sorption and Expansion of alkali reactive Silicas

Hirche, Ludwig and Wolff (4) pointed out that the alkali-silica reaction depends mainly on following physico-chemical phenomena:

1. Diffusion of alkali ions and calcium ions to the reaction site in the silica grain

   Alkali ions and calcium ions diffuse along silica interfaces. Alkali ions diffuse more rapid because of its smaller size ($K^{+}_{solv.} = 1.75$ Å, $Na^{+}_{solv.} = 2.17$ Å, $Ca^{++}_{solv.} = 2.75$ Å) and of the stronger electrostatical interaction of the calcium ions with the lattice atoms.

2. Ion exchange of alkali and calcium at silica interfaces

The diffused cations Na^+, K^+ and Ca^{++} exchange against the protons of the silanol groups. Na^+ and K^+ exchange reversible, Ca^{++} exchanges irreversible. Calcium hydro-silicates will be concentrated at external interfaces, because of the exchange of calcium ions against alkali ions, too. The released alkali ions are available for further reaction at internal interfaces. There should be a surplus of alkali ions at internal interfaces.

3. OH-ion action with the silica lattice

Normally the silica interfaces are covered with a second layer of H_2O. Hydroxyl ions diffuse with the solvated cations to the reaction site. A water molecule of the second layer will be absorbed in the hydrate shell of the cation. The silica interface will be free now for the action of OH-ions. The hydroxyl ions react with the silica lattice and the cation-silica complexes. New silanol groups will be produced for further reaction.

4. Water sorption at the reaction site

With the formation of alkali hydro-silicates at internal interfaces the chemical potential of water near the reaction site decreases. Water will be transported to internal interfaces until the hydro-silicate is dissocated completely. The volume increasing of the waterless silicate to the voluminous alkali silica gel produces an increasing pessure in the silica grain and the surrounding hydrated cement paste.

The water sorption of alkali silicates in flint was studied with thermogravimetry investigation. Most experiments were conducted on fine and coarse flint grains which were stored in alkaline solutions few days. In Figures 4,5 and 6 the weight loss of the flint grains is given as a function of the temperature.

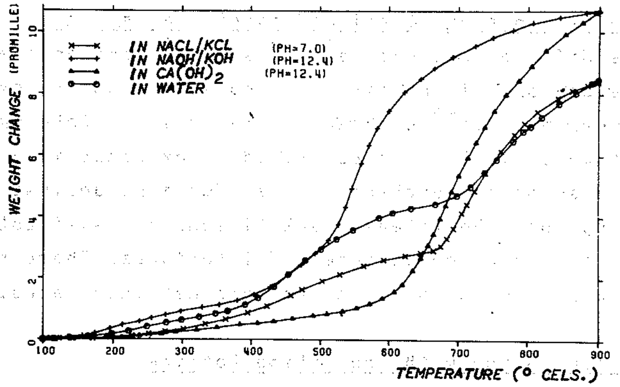

FIG. 4

Thermogravimetry of flint grains (grain size = 1.5-2.0 mm) stored in alkaline solutions

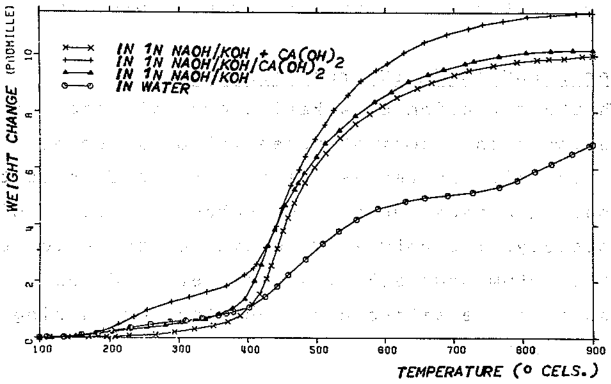

FIG. 5

Thermogravimetry of flint grains (grain size = 0.75-1.0 mm) stored in alkaline solutions

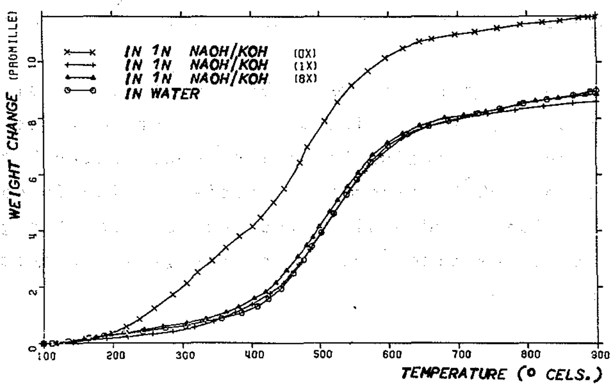

FIG. 6

Thermogravimetry of flint grains (grain size = 0.05-0.07 mm) stored in alkaline solutions

The results from these thermogravimetry investigations may be summarized as follows:

1. In presence of alkalis and OH-ions in solution the water sorption of flint grains increases (see FIG. 4). After heating in a vacuum the flint looses specially the bonded water between 500 °C and 600°C temperature.
2. In presence of calcium and OH-ions the water sorption of flint increases, too (see FIG. 4). The binding energy of water in calcium silicates is higher. The bonded water will be released between 650°C and 700°C temperature.
3. Storing the flint grains in an alkaliferous solution without OH-ions (= NaCl/KCl solution), one could not find any increasing water sorption.
4. Have we calcium ions in alkaline solutions the flint grains absorb water, too (see FIG. 5). The weight loss is similar to the measurements on flints stored in calcium free NaOH/KOH solution. Because of the small surface and of the short reaction time, the previously described ex-

change of calcium ions against alkali ions didn't occur (5).

5. The binding energy of water bonded at alkali silicate interfaces in fine flint grains is very low (see FIG. 6). The fine flint grains loose its bonded water between 200°C and 400°C temperature specially. The formation of the alkali hydro-silicates occured near the grain surfaces. One time flushing of the grains washed out all hydro-silicates.

Experimental procedure

All thermogravimetry investigations were made with an electro balance of Cahn-Instruments. The prepared flint grains were heated in a quartz tube under vacuum of 10^{-2} torrs. The heating temperature increased in steps of 2°C/min.

Before testing, the flint grains (0.05-0.07 mm, 0.75-1.0 mm and 1.5-2.0 mm) were stored 6 days in tridistillated water or in different alkaline solutions as follows:
NaOH/KOH solution (pH=12.4), $Ca(OH)_2$ solution (pH=12.4), 1n NaOH/KOH solution, 1n NaOH/KOH solution with addition of undissolved $Ca(OH)_2$, 1n $NaOH/KOH/Ca(OH)_2$ solution and NaCl/KCl solution (pH=7.0).

The flint specimens were contaminated partly through calcium carbonates. Heating calcium carbonates, we measure the releasing of CO_2 from 600°C to 900°C approximately. Due to the chemical analysis of the examined flint, we suggest that the different weight losses in the temperature range from 650°C to 900°C were caused partly through higher $CaCO_3$ contamination on the coarse flint grains. The maximum $CaCO_3$ contamination of flint minerals could be 0.80 percents in weight, the CO_2 contamination could be 0.35 percents in in weight.

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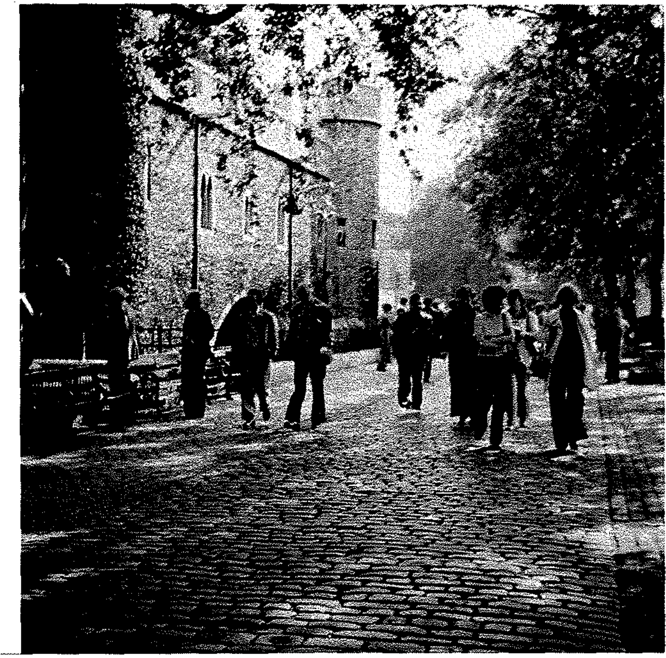

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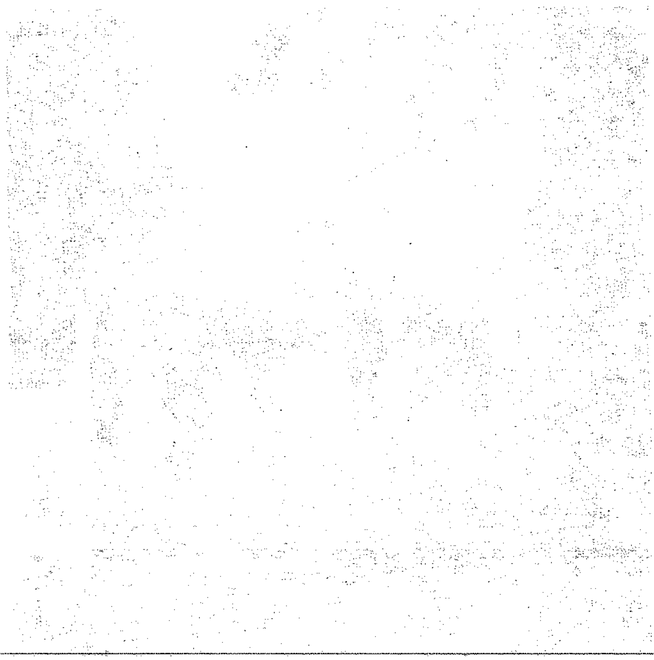

A PROSPECTIVE MEASURE FOR THE EXTENT OF ALKALI-SILICA REACTION

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ABSTRACT

Studies of alkali-silica reaction and its effects have been handicapped by the absence of a method of measuring the extent of the chemical reaction itself, as distinguished from measurement of the expansion. Expansion may or may not accompany reaction, depending on various factors. The proposed method involves determination of the alkali contents of pore solutions expressed from mortars in a special pressuring device operated at about 75,000 psi. After appropriate corrections, the reduction in the alkali concentration of pore fluid from reacting mortars as compared with pore fluid from companion mortars free of reactive silica is used to calculate the degree of reaction that has occurred and to estimate the amount of product formed. Illustrative data are provided for reactive mortars made with ground opal and hydrated for periods of up to 70 days.

INTRODUCTION

Interest in alkali-aggregate reactions in concrete is currently at a high level in view of the increased likelihood of deleterious responses stemming from increased levels of alkali contents in many cements and increased usage of marginal aggregates.

One of the major difficulties in understanding the details of alkali-silica reactions has been the inability of research workers to measure the extent and rate of reaction to be expected in a given reactive combination.

Tests of expansions with mortar bars provide appropriate measure of the expansion due to reaction, but not of the reaction itself. It is well known that many combinations of components will react, sometimes extensively, without giving rise to immediate expansion; in some circumstances the expansion does not take place at all. An independent measure of the extent of reaction, separate and distinct from measurements of expansion is clearly needed.

It is the purpose of this paper to present and illustrate progress in the development of such a measure.

BACKGROUND OF METHOD

In principle, most chemical reactions involve the combination of two or more reactants to produce one or more reaction products. The extent of reaction can be assessed by monitoring either the increasing concentration or amount of product or products, or the decreasing concentration or amount of one or more of the reactants.

In alkali-silica reactions the product is an alkali-silica gel of uncertain and variable composition located irregularly in patches within the body of the affected mortar or concrete. It is obviously not feasible to pick out all of these patches to determine the amount of product formed. Of the reactants, it is similarly infeasible to monitor the decrease in amount of reacting siliceous aggregate. Hydroxide ions in solution can be readily monitored, but the presence of a vast reservoir of easily mobilizable hydroxide ions in the form of solid calcium hydroxide disseminated throughout the hydrated cement paste complicates the use of this reactant as an indicator of the progress of the reaction. This leaves measurement of alkali cations, principally K^+ and Na^+,as the remaining possibility.

Fortunately, use of the alkali for concentration as an indicator of the extent of reaction has several favorable aspects. The alkali ions are readily mobile throughout the affected mortar or concrete, at least while saturated. Thus, while a uniform concentration of these ions throughout the mass cannot be guaranteed, it seems as this should reasonably be the case; if this is so the alkali concentration determined from a sample of pore fluid ought to be reasonably representative. Also, the alkali ions are relatively easy to determine by standard methods, once the solution has been obtained.

However, a number of features preclude the simple approach of using the reduction of alkali ion concentration with time as a measure of the extent of reaction. To begin with, alkali concentrations in mortars isolated from additional water supply increase with time as water is subtracted from the pore fluid by the processes of cement hydration. Secondly, at least in some cements, some of the alkalies are considerably delayed before reaching solution; thus later portions entering solution tend to mask alkali ions being withdrawn from solution by the alkali-silica reaction. Third, there is evidence that some of the alkali ions may enter solid solution within the C-S-H gel of the hydrated cement. Finally, there is the concept that some of the alkali may be "recycled" after reaction with silica, i.e., displaced by calcium to form a more stable calcium alkali silicate.

An approach has been evolved which seems to take care of all of these difficulties except perhaps the last. So far, no method has suggested itself by means of which the amount of "recycled" alkali returned to solution can be monitored. To the extent that this phenomenon occurs, the method illustrated here will underestimate the extent of alkali silica reaction recorded.

The method suggested involves measuring the concentrations of the alkali cations (Na^+ and K^+) in the pore fluid of reacting mortars or concretes and comparing these to corresponding measurements carried out on identical mortars or concretes "blank" with respect to silica that can take part in the reaction. Both measurements are corrected for the increase in concentration due to removal of water for cement hydration. The difference in the adjusted concentrations of alkalies between reacting mixtures and identically exposed "blanks" provides a quantitative index of the alkali consumed in the alkali-silica reaction. Further, an estimate of the amount of reactive silica consumed can be derived if an assumption as to the stoichiometry of the reaction product is made.

The remainder of this paper provides a detailed illustration of the application of this scheme to one series of specimens and of the conclusions that can be drawn from it.

EXPERIMENTAL DETAILS

A series of mortars were prepared using a moderately high-alkali ASTM Type I cement whose composition is given in Table I. "Blank" mortars incorporated cement, ASTM Designation: C 109 standard Ottawa sand, and water, in the weight proportions 1:2:0.5. Reacting mortars incorporated a ground reactive opaline silica ("Beltane opal" from Sonoma County, California) in the proportion of 10 percent by weight of the cement, with a portion of the sand removed so as to provide constant yield of mortar. The opal had been ground in a ball mill to a Blaine fineness of 11,000 cm^2/g.

The mortar specimens were cured in sealed containers at 20° C for periods from 1/2 hour to 70 days. They were then subjected to pressures of approximately 75,000 psi in a special pressuring device designed to facilitate extraction and recovery of pore fluid. Yields ranged from ca. 10 ml at early ages to less than 2 ml for more mature specimens, the fluid being collected in a syringe with only minimal exposure to the atmosphere. Details of the apparatus and collection procedure will be published elsewhere. The fluid recovered was immediately analyzed for alkali ions by flame photometry using a Perkin-Elmer Model 503 atomic absorption spectrophotometer flame photometer unit.

ALKALI CONCENTRATION IN "BLANK" MORTARS

From the cement analysis of Table I it is calculated that if all of the alkalies were to be dissolved in the mix water the resulting concentrations 75 would be 0.395 N for K^+ ions and 0.193 N for Na^+ ions, for a combined alkali ion concentration of 0.588 N. The concentrations of ions actually found to be present in the pore solutions of the non-reactive "blank" mortars are given in Table 2. The combined "raw" alkali concentration exceeds 0.588 N after about half a day and is very much higher after extended hydration. The effect is clearly due to withdrawal of water as it is incorporated in hydrating cement paste.

Unfortunately the non-evaporable water contents of the present specimens were not measured. In lieu of direct measurements, recourse was had to the "standard" non-evaporable water vs. age curve of Copeland and Kantro (1), and the combined water withdrawn from the pore solution was estimated for each specimen from their w:c 0.5 curve. The combined water was subtracted from the total water to yield an estimate of the residual fluid water at each age. The concentrations of alkali ions found at each stage were then adjusted by multiplying by the quotient of residual water divided by original water contents. This correction thus eliminates the effect of the removal of the hydration water and yields an equivalent concentration calculated on the basis of the original water content. The results of these calculations are also provided in Table 2.

The data provide some insight into the behavior of alkalies in hydrating cement and concrete notsubject to alkali-aggregate reaction. After the first half hour the K^+ ion concentration corrected for hydration water removal was within experimental error of the 0.395 N value expected if all of the potassium is dissolved, indicating that all of the potassium in this cement is readily hydrolyzable. The corrected Na^+ ion concentration was initially only about two-thirds of the corresponding 0.193 N value, although it increases somewhat up to a day. After several days there is a slight but definite decline in the corrected K^+ concentration, and some irregular reduction in Na^+. We consider that this reduction likely represents slow incorporation of the alkalies into the C-S-H gel; alternatively, some of it may represent reaction with the "non-reactive" quartz sand.

The trend indicated is illustrated in Fig. 1, in which the "corrected" concentrations of combined alkalies are expressed as percentages of the total alkali content provided by the cement, and plotted vs. time. Apparently with this cement about 90 percent of the alkali present is mobilized immediately; the amount in solution increases slightly between half a day and a day; and subsequently there is a gradual reduction to about 80 percent of the total in about two months.

ALKALI CONCENTRATIONS IN REACTING MORTARS

The actual K^+ and Na^+ concentrations found in the solutions expressed from the sealed reactive mortars are given in Table 3, along with the corresponding values corrected for the withdrawal of water by cement hydration. The corrected K^+ concentrations are maintained at close to the 0.395 N value for the first half day or so, and then drop steadily and progressively to a low of 0.200 N at 70 days, reflecting the early onset and progress of the alkali-silica reaction. The corresponding Na^+ results are less clearly defined, but appear to show a modest decrease starting at about 4 days.

QUANTITATIVE ASSESSMENT OF EXTENT OF REACTION

The amount of alkali tied up in alkali-silica reaction product, i.e., the desired estimate of the extent of the reaction, is calculated from the difference between the corrected concentrations of the alkalies between "blank" and reacting specimens of a given age. The data are given in Table 4, for each of the alkali ions. The combined tally is re-expressed as a percentage of the total alkali provided by the cement, and plotted against time in Fig. 2.

The results indicate that about 3 percent of the total alkali present has reacted almost immediately; that about 6 percent has reacted by 1 day, about 23 percent by 1 month, and 28 percent by about 2 months. The inset shows the detailed time trend for the first day. Early data can be fitted reasonably well to linear plots on both log time and square root of time plots, but later data depart significantly from the trends.

With an additional assumption about the stoichiometry of the reaction product one can form some idea about the proportion of the reactive silica that has reacted in a given time. Krogh (2) recently summarized published data on analyses of alkali-silica reaction gels. The $(K_2O + Na_2O / SiO_2)$ mole ratios reported range from virtually zero to 0.40; but neglecting four obviously aberrant analyses showing values of 0.06 and below, the average

TABLE 2

ANALYSIS OF ALKALI ION CONCENTRATIONS IN PORE SOLUTIONS EXPRESSED FROM "BLANK" MORTARS

	K^+ Ion Conc. N		Na^+ Ion Conc. N		$Na^+ + K^+$ Conc.	Correction
Age	Original	"Corrected"	Original	"Corrected"	(Corrected)	Factor*
1/2 Hour	0.405	0.397*	0.134	0.131	0.528	0.98
1 Hour	0.405	0.389	0.135	0.130	0.519	0.96
3 Hours	0.412	0.395	0.136	0.131	0.526	0.96
6 Hours	0.424	0.399	0.144	0.135	0.534	0.94
14 Hours	0.474	0.427	0.163	0.147	0.574	0.90
27 Hours	0.496	0.396	0.197	0.157	0.553	0.80
4 Days	0.547	0.383	0.201	0.141	0.524	0.70
9 Days	0.532	0.341	0.204	0.131	0.472	0.64
15 Days	0.554	0.344	0.215	0.133	0.477	0.62
49 Days	0.594	0.356	0.242	0.145	0.501	0.60
70 Days	0.575	0.333	0.218	0.126	0.459	0.58

*Corrected for water withdrawal due to hydration of the cement; correction factor for any given age is $\frac{\text{Total Water - Estimated Non-Evaporable Water}}{\text{Total Water}}$

TABLE 3

ANALYSIS OF ALKALI ION CONCENTRATIONS IN PORE SOLUTIONS EXPRESSED FROM REACTING MORTARS

	K^+ Ion Conc., N		Na^+ Ion Conc., N		Combined $(K^+ + Na^+)$ Conc., N
Age	Original	Corrected*	Original	Corrected*	Corrected*
1/2 Hour	0.394	0.386	0.126	0.124	0.510
1 Hour	0.392	0.376	0.123	0.118	0.494
3 Hours	0.394	0.378	0.126	0.121	0.499
6 Hours	0.407	0.383	0.135	0.127	0.510
14 Hours	0.445	0.401	0.148	0.133	0.534
27 Hours	0.454	0.363	0.190	0.152	0.515
4 Days	0.468	0.328	0.173	0.121	0.449
9 Days	0.442	0.283	0.153	0.098	0.381
15 Days	0.447	0.277	0.197	0.122	0.399
49 Days	0.384	0.230	0.186	0.112	0.342
70 Days	0.345	0.200	0.170	0.099	0.299

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*For correction factors, see Table 2.

TABLE 4

DIFFERENCE BETWEEN CORRECTED CONCENTRATIONS OF "BLANK" AND REACTING MORTARS

Time	Difference in K^+ Conc., N	Difference in Na^+ Conc., N	Total Difference N
1/2 Hour	0.011	0.007	0.018
1 Hour	0.013	0.012	0.025
3 Hours	0.017	0.010	0.027
6 Hours	0.016	0.008	0.024
14 Hours	0.026	0.014	0.040
27 Hours	0.033	0.005	0.038
4 Days	0.055	0.020	0.075
9 Days	0.058	0.033	0.091
15 Days	0.067	0.011	0.078
49 Days	0.126	0.033	0.159
70 Days	0.133	0.027	0.160

TABLE 5

CALCULATIONS OF AMOUNTS OF REACTIVE SILICA CONSUMED IN ALKALI REACTION

Time	*Total Ion Concentration Difference, N	**Calc. No. of Moles of Alkali Ions Reacted per g of Reactive Silica Added to Mortar	***Corresponding No. of Moles of SiO_2 in Reaction Product	Calculated Percentage of the Reactive Silica Added to Mortar that has Reacted
1/2 Hour	0.018	0.000090	0.00072	4.3%
1 Hour	0.025	0.000125	0.00100	6.0
3 Hours	0.027	0.000135	0.00108	6.5
6 Hours	0.024	0.000120	0.00096	5.8
14 Hours	0.040	0.000200	0.00160	9.6
27 Hours	0.038	0.000190	0.00152	9.1
4 Days	0.075	0.000375	0.00300	18.0
9 Days	0.091	0.000455	0.00364	21.9
15 Days	0.078	0.000390	0.00312	18.7
49 Days	0.159	0.000795	0.00636	38.2
70 Days	0.160	0.000800	0.00640	38.5

*Difference in corrected alkali concentrations of "Blank" and "Reacting" Mortars of the same age, from Table 4.

**Reactive silica added at the rate of 10% by weight of cement used, hence ratio is 5 ml of water present per g of reactive silica.

***Assuming $\frac{K + Na}{Si}$ mole ratio is 0.125, corresponding to $\frac{K_2O + Na_2O}{SiO_2}$ mole ratio of 0.25.

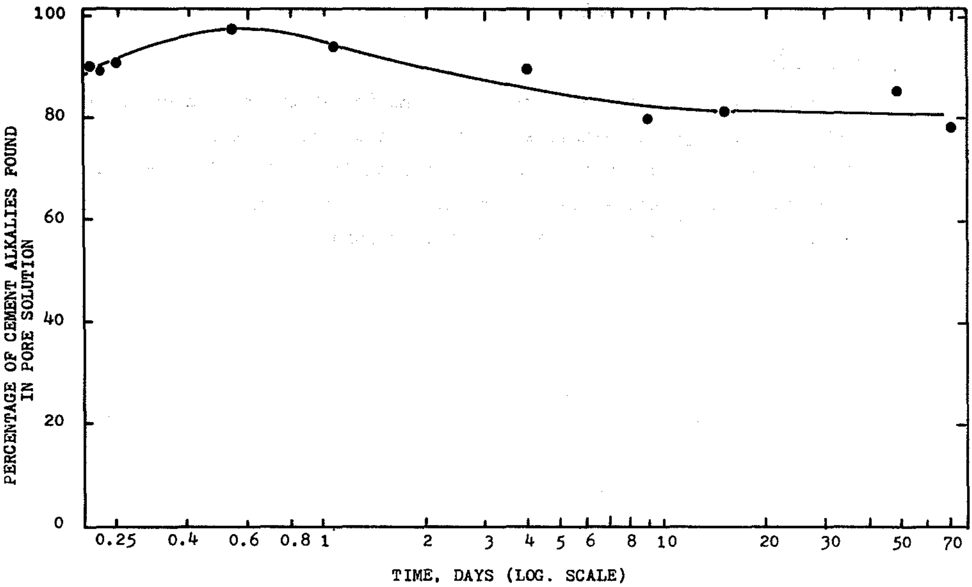

Fig. 1. Combined alkali contents of "blank" mortar pore solutions expressed as percentages of total alkalies present.

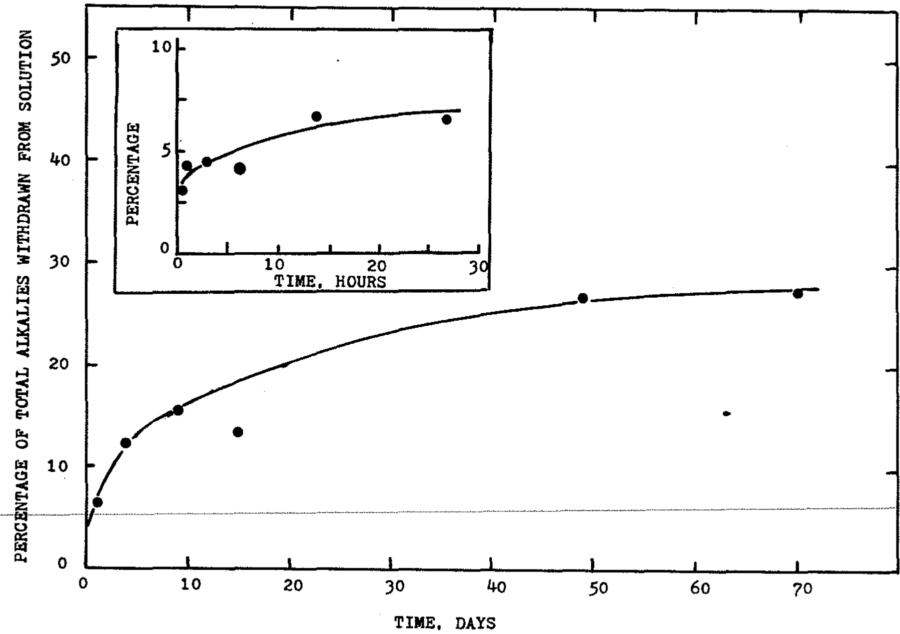

Fig. 2. Calculated percentage of the total alkalies that has been withdrawn from solution as alkali-silica reaction product.

CONTRIBUTION TO DISCUSSION

Dr. D. Hirche

A great problem is to get correct information about the ion exchange of Ca^{++} ions against alkalies in the reaction time. We know that this exchange occurs mainly on the outer surfaces of silica grains. Because of the great surface area (11000 approximately) of the tested opal we have to be careful on this point.

ELECTRON PROBE MICROANALYSES OF REACTION ZONES AT CEMENT/OPAL INTERFACES

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ABSTRACT

Small rectangular prisms of Beltane Opal embedded in ordinary portland cement, and cements containing 2% and 6% of NaCl were prepared in the laboratory and stored at 40°C for 7 and 28 day periods. Microscopic examination and electron probe microanalyses of reaction zones developed near the interface show that the reaction zone develops within the opal and is a composite of two or three optically distinct regions. The width of the zone increases with time and varies with the alkali content of the cement, the cement containing 2% NaCl giving the widest reaction zones. The variation of sodium and potassium as well as certain other elements across the reaction zone changes with time, but their variation is also partly dependent on the levels of sodium chloride present in the cement.

Introduction

Since the work of Stanton[1] in 1940 a considerable volume of research work has been published concerning the nature and effects of alkali-silica reaction in concretes, and case studies have been reported from many parts of the world. As researches have progressed the mechanism of the reaction has become better understood, and the suggestion of pessimism proportions for maximum expansive reaction made by Mielenz et al[2] and recently clarified and elaborated by Ozol[3] has become an important consideration in present researches. Detailed investigations of the reaction zone between the aggregate and cement paste such as those carried out by Thaulow and Knudsen[4] have provided further information on the details of the reaction processes but have in their turn raised further problems which require explanation.

In reports of some case-study investigations it is clear that alkali-silica reactivity combines with other factors such as sulphate or chloride contamination of the aggregates to produce the deleterious effects observed.[5] 76 These observations raise the possibility that the alkali-silica reaction may be modified by interaction with other reactions and processes taking place in the concrete at the same time. Alkali-silica reactivity has been reported in a number of case studies from Mediterranean and Middle Eastern countries[5,6,7] and a further example from Das Island in the Arabian Gulf is currently under investigation. The wide temperature and humidity fluctuations in these countries appears to accelerate the deleterious processes; and aggregates contaminated by chlorides or sulphates which are not uncommon in this region present a problem for the construction engineer.

In order to begin to investigate some of these problems in the laboratory a series of samples were prepared using a reactive low cristobolite opal set in cements to which sodium chloride had been added. After a storage period the progress of the alkali-silica reaction was monitored using an electron probe microanalyser.

Experimental Procedures

The specimens used in this study were prepared from 10mm by 7mm rectangular tablets of Beltane Opal which were 2mm thick. These tablets were embedded in a cement paste with a water/cement ratio of 0.4. After a curing period of 24 hours at 20°C the small specimen blocks were stored over water in pairs in sealed containers at 40°C. Specimens 1 and 2 were stored together and prepared using ordinary portland cement with total alkalies 0.54%. Specimens 3 and 4 stored together had 2% by weight analar sodium chloride added to the cement at time of manufacture. Specimens 5 and 6 were similar to 3 and 4 but with a 6% addition of sodium chloride. The analyses of the cement, and a partial analysis of the opal used are given in Table 1.

TABLE 1

Analyses of cement and opal used in this study

	Portland Cement	Beltane Opal
SiO_2	20.2	-
Al_2O_3	7.2	0.33
Fe_2O_3	2.2.	-
Mn_2O_3	0.04	-
P_2O_5	0.16	-
TiO_2	0.33	-
CaO	64.1	0.12
MgO	1.3	-
SO_3	2.7	-
K_2O	0.41	0.12
Na_2O	0.13	0.10
L.O.I.	0.8	-
I.R.	0.33	-

Specimens 1, 3 and 5 were removed from storage after 7 days, dessicated, impregnated with araldite and prepared as petrographic thin sections suitable for electron probe microanalysis. Specimens 2, 4 and 6 were similarly treated after a storage period of 28 days. A summary of the specimen numbering scheme is given in Table 2 below.

TABLE 2

Test specimen numbering scheme

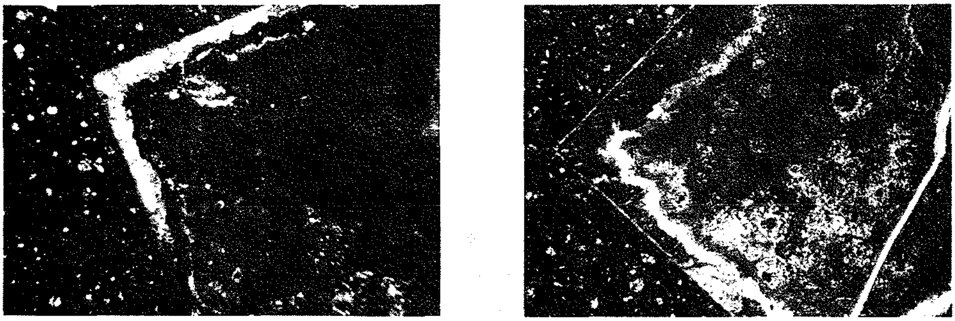
Type of cement used		7 days storage	28 days storage
O.P.C.	w/c 0.4	Specimen 1	Specimen 2
O.P.C. + 2% NaCl	w/c 0.4	Specimen 3	Specimen 4
O.P.C. + 6% NaCl	w/c 0.4	Specimen 5	Specimen 6

The prepared petrographic thin sections were examined and suitable portions of reaction zone selected for electron probe microanalysis. The microanalyses were carried out using the non dispersive electron probe in the Department of Mineralogy, Cambridge. This instrument is linked to a small computer which allows spectrum stripping and correction procedure programmes to be applied to the X-ray results. The instrument provides complete analyses of 5 to 10 micron diameter areas which can be selected optically. Numerous spot analyses were made along approximately linear traverses from the cement paste through the reaction zone and into the opal.

Results

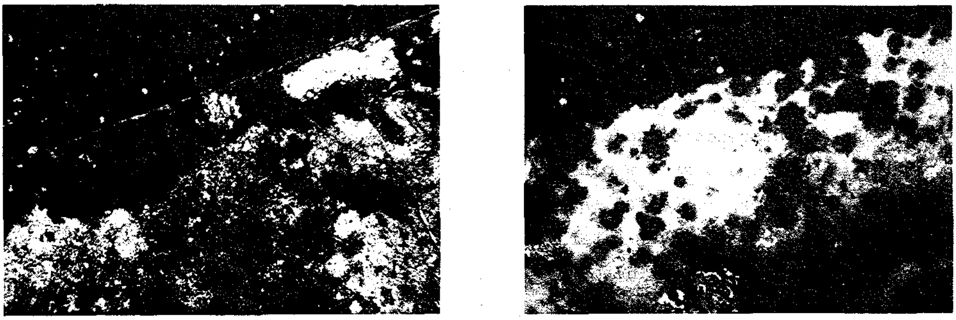
Petrographic examination of the specimens clearly shows that the reaction zones lie entirely within the opal and appear to have developed after the cement had set. The reaction rims themselves were seen to consist of several zones. The cloudy irregular zone extending inwards for 2mm noted by Thaulow and Knudsen[4] was only clearly seen in specimen 1. However, a consistent feature of all the specimens was the development of a dark irregular zone at the inner part of the rim as seen under transmitted light. As a result of the high storage temperatures gels developed within the reaction rim tended to escape along cracks so that the specimens stored for 28 days had patchy developments of reaction product and void areas in the reaction rim areas nearest to the cement. Some of these features may be seen in the photomicrographs in Figure 1. These photomicrographs show typical areas of reaction rim and were taken in plane polarized transmitted light. The most obvious feature of the rims developed in the 6 specimens is their width variation. As expected the rims increase in size with time, and in all cases they approximately double in width under the storage conditions noted above during the 21 day interval selected in this study. It is interesting to note the comparison ofthe 150 micron rim developed after 8 months storage at room temperature reported by Thaulow[4] using a cement with 2.02 alkalies, and the 100 micron rim developed after 7 days at 40°C with a 0.54 alkali cement in specimen 1. A second feature of importance is that the specimens containing 2% of added sodium chloride exhibit wider reaction rims than those containing 6% sodium chloride.

The petrographic sections were coated with carbon and between 10 and 17 individual analyses were made on each sample along a traverse perp-



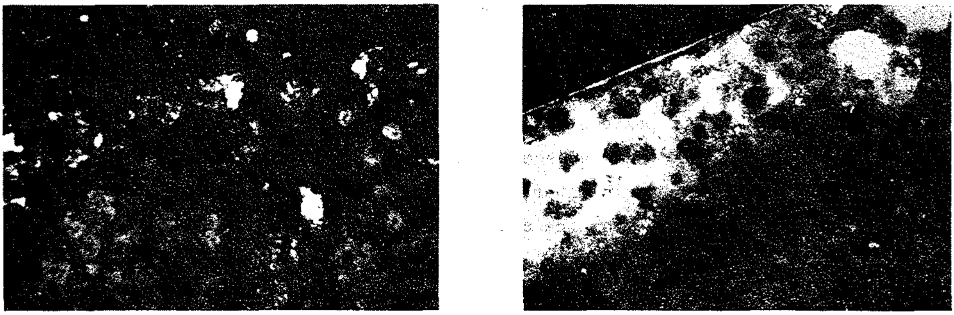
Specimen 1

Specimen 2



Specimen 3

Specimen 4



Specimen 5

Specimen 6

Fig.1
Photomicrographs of the 6 specimens used for electron probe microanalysis
The width of the field of view is 2.0mm

endicular to the interface from the cement through the reaction zone and into the unaltered opal. Of these analyses 7 were selected from each specimen and are recorded in Tables 3, 4 and 5. The additional analyses confirm that the analyses shown here are typical of the particular area in the specimen from which they come. The porous zones and void areas in the wider reaction rims were avoided so that analyses from the central part of these rims reflect the composition of the solid reaction product materials in those areas. The analyses tabulated show typical compositions of small areas in the specimens as indicated in the key to analyses. The particular spots chosen for the individual analyses appeared to be homogeneous in transmitted and reflected light but clearly must represent the composition of only the few mineral grains at the focus of the electron beam. As is to be expected the greatest variation between closely spaced analyses was observed in the cement paste areas.

The analytical results given in Tables 3, 4 and 5 have a number of features of interest, silica typically shows a gradual increase from the front of the reaction zone to the back and into unaltered opal, though specimens 2 and 3 show a minimum in the central region of the rims. These minima are also reflected in lower totals for these particular analyses and may indicate higher water contents. With the exception of specimens 1, 5 and 6 no iron was detected as having migrated into the rims and in even these specimens it was only present in the outermost rim zones. Magnesium similarly does not easily enter the reaction zone, the outermost part of the very narrow zone in specimen 1 being the only exception.

TABLES 3, 4 and 5

Electron Probe Spot Microanalyses across cement/opal reaction zones

Key to Analyses

1. Cement paste at a distance of more than 1mm from the opal
2 Cement paste adjacent (within 0.01mm) to the reaction rim
F Reaction rim material close to the cement interface
C Material from the central zone of the reaction rim
B Material from the inmost part of the visible reaction rim
3 Material adjacent to but just beyond the visible reaction rim
4 Material from the central part of the opal prism
* Total Iron as Fe_2O_3
** Water and CO_2 are not determined by this method

TABLE 3

Specimen 1 Width of Reaction Rim 0.10 mm

%	Cement		Reaction Rim			Opal	
Oxide	1	2	F	C	B	3	4
SiO_2	13.84	17.07	29.99	74.10	76.18	94.22	94.99
Al_2O_3	1.77	2.77	3.55	0.68	0.33	0.00	0.22
$Fe_2O_3^*$	0.60	0.45	0.97	0.00	0.00	0.00	0.00
MgO	0.31	0.66	1.01	0.00	0.00	0.00	0.00
CaO	57.79	51.77	47.04	4.44	0.63	0.25	0.14
Na_2O	0.00	0.00	0.00	1.69	0.80	0.00	0.00
K_2O	0.00	0.00	0.00	3.55	0.81	0.42	0.00
S	0.74	2.15	2.73	0.51	0.28	0.19	0.00
Cl	0.00	0.00	0.00	0.09	0.00	0.00	0.00
Total**	75.05	74.87	78.29	85.06	79.03	95.08	95.35

Specimen 2 Width of Reaction Rim 0.25 mm

%	Cement		Reaction Rim			Opal	
Oxide	1	2	F	C	B	3	4
SiO_2	19.37	17.68	70.62	64.56	89.37	97.10	94.35
Al_2O_3	2.74	9.61	0.71	0.00	0.83	0.38	0.23
$Fe_2O_3^*$	0.66	3.58	0.00	0.00	0.00	0.00	0.00
MgO	0.76	1.07	0.00	0.00	0.00	0.00	0.00
CaO	51.58	41.62	0.34	0.11	0.14	0.00	0.00
Na_2O	0.00	0.00	0.52	0.42	0.49	0.00	0.00
K_2O	0.00	0.14	0.18	0.60	0.45	0.40	0.28
S	1.02	1.87	0.00	0.00	0.00	0.00	0.00
Cl	0.00	0.36	0.14	0.15	0.00	0.00	0.00
Total**	76.13	75.93	72.51	65.84	91.28	97.88	94.86

TABLE 4

Specimen 3 Width of Reaction Rim 0.60 mm

%	Cement		Reaction Rim			Opal	
Oxide	1	2	F	C	B	3	4
SiO_2	21.21	19.03	51.24	49.62	78.18	92.61	96.38
Al_2O_3	3.39	2.97	0.30	0.21	0.40	0.30	0.00
Fe_2O_3*	0.94	0.55	0.00	0.00	0.00	0.00	0.00
MgO	0.75	0.36	0.00	0.00	0.00	0.00	0.00
CaO	46.56	47.10	3.01	0.39	0.35	0.20	0.20
Na_2O	0.00	0.00	2.52	1.80	1.78	1.27	0.00
K_2O	0.00	0.23	1.32	0.38	0.94	0.46	0.00
S	3.18	3.14	0.00	0.00	0.00	0.00	0.00
Cl	1.27	0.85	0.19	0.17	0.00	0.09	0.00
Total**	77.30	74.23	58.58	52.57	81.65	94.93	96.58

Specimen 4 Width of Reaction Rim 1.60 mm

%	Cement		Reaction Rim			Opal	
Oxide	1	2	F	C	B	3	4
SiO_2	23.02	22.99	70.38	73.33	88.18	96.27	95.24
Al_2O_3	2.66	4.99	0.23	0.00	0.00	0.40	0.49
Fe_2O_3*	0.41	0.66	0.00	0.00	0.00	0.00	0.00
MgO	0.28	0.68	0.00	0.00	0.00	0.00	0.00
CaO	42.61	43.78	5.65	0.14	0.11	0.00	0.00
Na_2O	0.00	0.46	3.52	1.72	1.75	0.92	0.38
K_2O	0.09	0.00	2.30	0.93	0.82	0.36	0.16
S	3.40	4.34	0.18	0.34	0.00	0.00	0.00
Cl	0.71	1.27	0.12	0.10	0.00	0.00	0.00
Total**	73.18	79.17	82.38	76.56	90.86	97.95	96.26

TABLE 5

Specimen 5 Width of Reaction Rim 0.55 mm

%	Cement		Reaction Rim			Opal	
Oxide	1	2	F	C	B	3	4
SiO_2	10.06	15.92	8.93	55.75	72.48	90.91	91.99
Al_2O_3	2.20	5.15	1.31	0.44	1.37	0.23	0.29
Fe_2O_3*	0.35	0.46	0.18	0.00	0.00	0.00	0.00
MgO	0.49	0.48	0.00	0.00	0.00	0.00	0.00
CaO	57.76	39.44	54.06	0.37	0.27	0.20	0.15
Na_2O	0.46	1.24	0.63	7.96	3.01	1.46	1.09
K_2O	0.00	0.32	0.10	0.68	0.92	0.33	0.13
S	2.08	3.61	1.37	0.23	0.00	0.00	0.00
Cl	1.52	2.68	1.28	0.17	0.12	0.25	0.36
Total**	74.92	69.30	67.86	65.60	78.17	93.38	94.01

Specimen 6 Width of Reaction Rim 0.90 mm

%	Cement		Reaction Rim			Opal	
Oxide	1	2	F	C	B	3	4
SiO_2	9.67	13.38	27.14	75.90	89.34	95.97	93.56
Al_2O_3	11.56	7.69	2.11	0.21	0.66	0.00	0.23
Fe_2O_3*	3.05	2.76	0.18	0.00	0.00	0.00	0.00
MgO	0.66	1.11	0.00	0.00	0.00	0.00	0.00
CaO	41.65	43.91	45.77	1.22	0.37	0.22	0.33
Na_2O	0.00	0.00	1.85	3.32	1.19	0.55	0.65
K_2O	0.00	0.14	0.47	1.25	0.22	0.15	0.11
S	3.37	4.09	1.01	0.00	0.22	0.00	0.00
Cl	3.84	3.04	1.73	0.12	0.00	0.17	0.14
Total**	73.80	76.12	80.26	82.02	92.00	97.06	95.02

Calcium however does appear to be present in concentrations above that in the opal in all reaction rims and the pattern is consistent for all specimens. In the very outermost zone of the reaction rim CaO is present in amounts comparable with the adjacent cement paste, but within a few microns of the interface the concentration drops to a few percent and in the back part of the rim zone the concentration levels are only a little higher than the trace amounts found in the opal. Although the detection limit for sodium is about 0.1% (as Na_2O) it is interesting to note that only sample 5 has sodium present in the cement at a distance from the interface. Several specimens contained areas with K_2O present in trace amounts within the cement paste, though there is also some evidence to suggest that Na_2O and more especially K_2O tend to become concentrated in the cement pastes adjacent to the interface and this effect is best shown by specimen 5 in these results.

The concentration of both sodium and potassium in the reaction zones is very obvious from the tables. The variations across and beyond these reaction zones are illustrated in Figure 2. These diagrams show how the alkalies are distributed within the reaction zones and how the concentration levels change with time. Specimens 1 and 2 clearly show a dissipation of the alkalies as the reaction rim widens, while specimens 3 and 4 show a build up of both sodium and potassium in the rim over the 28 day period. Specimens 3 and 4 with 2% added sodium chloride contrast with 5 and 6 (6% added NaCl) in that these last two specimens show that sodium increases to very high concentrations in the rim at first but reduces with time. However, the potassium in 5 and 6 does not reflect the change in concentration shown by the sodium in the way that it does in 3 and 4.

Discussion

If the addition of sodium chloride is regarded only as a straightforward addition of sodium ions to the cement, then these experiments would appear to indicate that the pessimism for alkalies in this cement with the opal used and the storage conditions of these experiments would lie between 0.5 and 3.7% total alkalies as oxides. However, the addition of sodium chloride causes complex changes in the formation of the cement minerals. As an example X-ray diffraction results show that the development of calcium hydroxide is modified by the addition of salt. Although under the conditions used in this work calcium hydroxide formation is

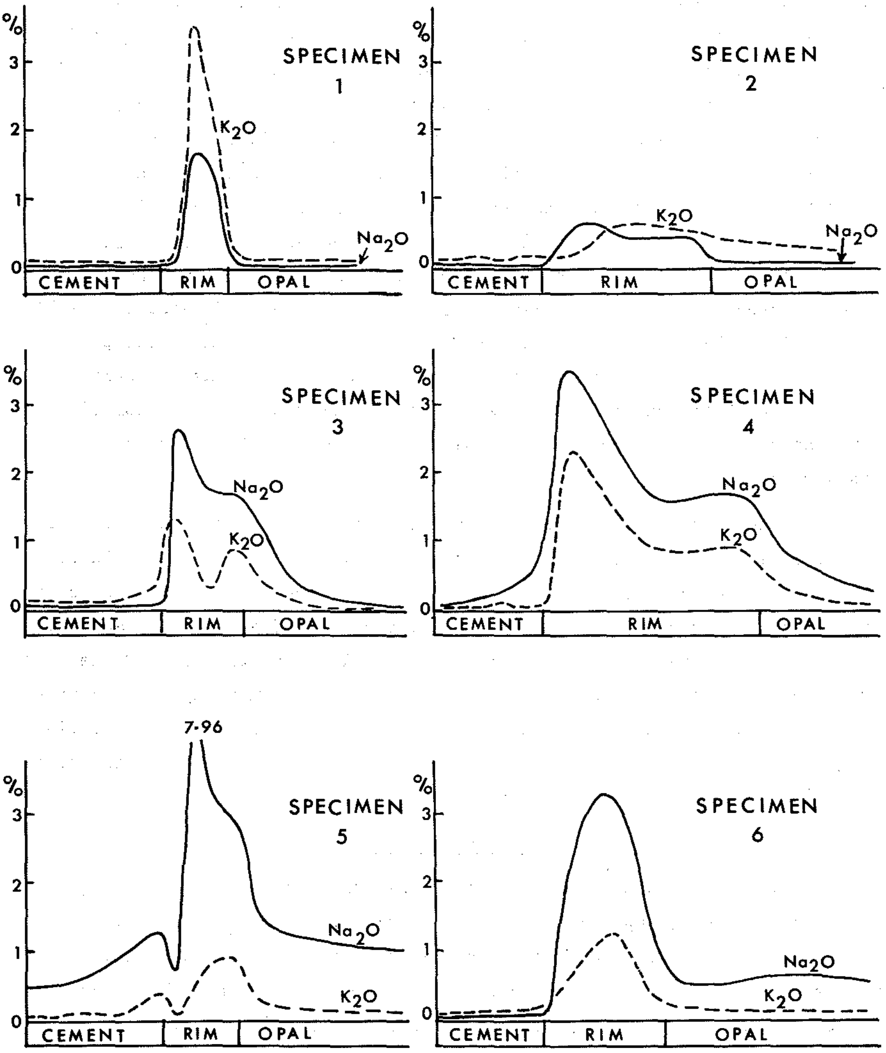


Fig. 2

Alkali variation across reaction zones

virtually complete after 7 days storage for the normal cement, calcium hydroxide is still developing at 28 days in the cements containing sodium chloride and this retardation is most marked in the specimens containing 6% additional sodium chloride. The addition also introduces chlorine to the cement, this is at first taken up in forming $C_3A(CaCl_2)H_{10}$ and similar minerals but chlorine ions are also absorbed onto the hydrates and to a lesser extent on unhydrated phases. Up to about 5% sodium chloride the chlorine can be accounted for in this way but at higher concentrations free sodium and chlorine ions may be present in pore solutions and halite may be detected in the dry cement paste. The presence of these ions will also affect the concentration of other ions notably calcium in the pore solutions and since the alkali-silica reaction progresses as a result of alkali ions being carried to the silica at the reaction site in solution any change in ionic concentrations will be reflected the progress of this reaction.

The results show that maximum local concentrations of sodium ions occur close to the reaction site within the opal reaction zones in these specimens, and as a result of these local high concentrations some calcium ions must be removed from solution[8]. The analyses of specimens 5 and 6 in particular show very high concentrations of calcium at the edge of the reaction zone and this insoluble calcium phase may form a physical barrier to the further movement of alkalies towards the reaction site thus providing an explanation for the reduced reactivity of specimens containing high alkali concentrations of this type.

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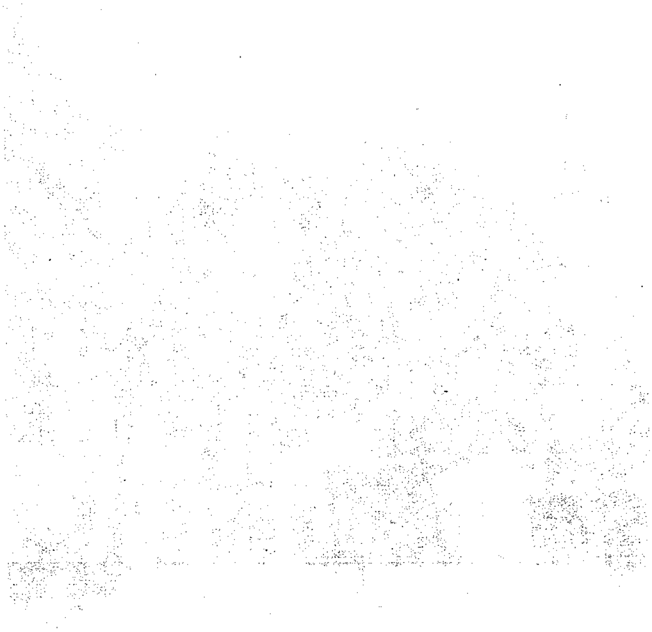

THE ROLE OF SOLVENT MIGRATION IN ALKALI-SILICATE REACTIVITY

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ABSTRACT

Solvent migration is considered as an alternative to diffusion for the transport of material towards reactive silicate fragments. Cement paste is viewed as being composed of an inert phase and a mobile phase. The former includes the cement hydrates and sulphates and the latter consists of excess water and more soluble elements such as the alkalies though the precise location of particular ingredients is likely to vary from time to time in the evolution of the concrete. Migration of the mobile phase follows the release of hygroscopic silicon into the paste surrounding reactive aggregate fragments and the flow of the mobile phase effects a chromatographic transfer of ions in the direction of flow. The position of bands of high concentration of mobile ions depends upon the distribution coefficients of the species between the inert and mobile phases. Alkalies are concentrated into the mobile phase and are therefore transmitted with the solvent front. The position of this alkali front is dependent on the mass ratio of the mobile to the inert phases; the higher this ratio the closer is the peak concentration of the alkalies to the aqueous front. The height of this peak is directly proportional to the mass of alkali in the cement system. Formulae are given that describe the possible form of the distribution of concentration along the length of the flow in the most simple circumstances. These formulae are applied in approximation to the aggregate-cement reaction and it is shown that the estimated curves are of similar dimensions to those found experimentally. The process of solvent migration may also take place in other deleterious reactions such as alkali-carbonate reaction and reinforcement corrosion. It is suggested that simple tests may be developed permitting the detection of the propensity of aggregate for creating the solvent flow. Prevention of this flow is germinal to the prevention of reaction and if solvent migration is of significance then the single most important factor in reducing reactivity will be reduction of excess water.

Introduction

This paper puts forward a tentative model for alkali-aggregate reaction which may account for some of the complexities of the reaction zones. The model leads to suggestions for tests for reactivity and should itself be capable of test. The paper owes much to the symposium volume from last years meeting in Iceland and also rests in part on experiments carried out more recently by the author's colleagues A.B. Poole and A.Baker, who have examined the chemical variations found around opal and 'non-reactive' quartz in experimental concretes.

A basic problem presented by both this new data and that given for example by Thaulow and Knudsen (1) is the complexity of elemental distribution in the reaction zones. Even in simplified experimental concretes with regularly shaped aggregate pieces the distribution of alkalies, for example, may be discontinuous and in some parts of the gel zones there may be no alkali while nearby the concentration may be nearly two orders of magnitude greater than that found in the paste. It is common to appeal to some kind of diffusion process to account for this accumulation of ions in the vicinity of the aggregate and this is epitomised by statements made by Vivian (2) that for alkali-silicate reactivity to occur hydroxyl and metal ions have to diffuse to the silica surface and that the slow rate of accumulation of reaction products is attributable to the slow rate of ion diffusion. This diffusion process is selective in being able to pick out specific aggregate particles for reaction. Shells develop around certain reactive fragments even where these are but a small fraction of the aggregate. How then do the hydroxyl and metal ions choose the right fragment? What is the drive for this diffusive process?

In general the water and alkali concentrations in the gel zones may reach very high levels and the gels may locally become as high as 3 or 4M in alkalies. At these high spots the concentration is then several times that found in the pore fluid of the cement (3,4) and several times again that of the original cement. The diffusion of alkalies is thus creating a concentration gradient up which further ions must climb. This may perhaps suggest that the material being formed is energetically more stable than the starting materials and that the gelatinous reaction product is analogous with a new crystalline phase appearing as the result of reaction between less stable solids or liquids. It is obviously not possible to argue that diffusion is directed by a concentration gradient for the levels achieved in the reaction zone are greater than those in the environment. Nor can a temperature gradient be postulated and paradoxically diffusion is occurring against a growing pressure. Moreover diffusion generated by chemical potential gradients cannot provide discontinuities or plateaux in the distributions of the chemical potentials and, unless there are temperature or pressure discontinuities the concentrations cannot be discontinuous either (5). Further, diffusion concentration profiles are usually of gaussian or high order binomial form and in general they will show different species migrating in different directions. The diffusion model cannot therefore readily account for the variability in composition of the reaction zones. Some of this variability may of course be analytical but there is sufficient evidence now available to justify the belief that the compositional variations are real.

An alternative to the diffusion model is that of solvent migration. This is directly analogous with chromatography in that what is required is an inert phase through which a solvent can migrate; a mobile phase able to reach local equilibrium with the inert phase; and a mechanism for causing the mobile phase to migrate through the inert. For the present reaction the stable cement hydrates and sulphates constitute the inert phase and the aqueous fluid of the interstices of the cement paste is the mobile phase. This aqueous fluid then largely corresponds with the water in excess of that required by stoichiometry for the cement hydrates and is largely held within pores, attached loosely to the surfaces of the solid materials or dispersed through paste gels. The composition of this hydrous phase is likely to vary considerably throughout the development of the concrete but will evidently hold much of the alkali content of the paste.

Undoubtedly in alkali-silicate reaction water and alkalies migrate to the aggregate but the cause of the migration is less readily identified. The migration of ions to specific aggregate fragments (and not to others) shows that it is the aggregate itself which controls or causes the motion of ions. The alkalies and water must of course be present but the initiation and probably the rate of the reaction must be governed by specific properties of the aggregate. Experiments with opal have shown that the gel is produced almost wholly within the aggregate and that as well as the water and alkalies, magnesium and calcium may also penetrate into the opal.

It is also well known that the aggregates have relatively high solubility in alkaline fluids compared with more stable material (6), and it could be argued that it is this solubility that controls the reactivity. The solubility will be influenced by many factors but for each aggregate the result will be that silicon atoms are released into the surrounding paste and into pores within the aggregate. It is therefore possible that the slow release of hygroscopic silicon atoms creates the necessary attraction for the hydrous mobile phase of the paste. Other ions are then released into the reaction zone as a consequence of this flow, and it is important that this mechanism collects the transported ionic species into sharply defined bands which may achieve very high concentration. The precise form of the distribution of concentration will depend on the adsorption isotherm of the system but it is shown below that it is possible to estimate the expected forms of the zones for simple 'ideal' systems. In general, the profile of these solute-rich bands is roughly gaussian with the flow mechanism tending to concentrate the solute into a very narrow band while the developing concentration contrast induces diffusion away from the position of maximum concentration.

Hence the essence of the present proposal is that reactive aggregate slowly produces by diffusion a high concentration of silicon atoms in its environment. This creates an attraction for the water of the paste and causes this pore fluid to migrate slowly towards the aggregate. Soluble ions are carried in the flowing fluid to produce sharply defined zones of high concentration near the aggregate fragments or within their decay products. The formation of first silica gel and then alkali-silicate gel continues to promote the influx of water and hence additional alkalies. This process goes on until the gel becomes mobile and in fact leaves the site of generation. The formation of the alkali-silicate gel does not itself inhibit reaction because, as experiments made by the author and A. Baker have shown, aggregates such as opal are appreciably soluble in sodium silicate gel. Movement of the gel away from the source of silicon may then permit reverse migrations, for, the high concentrations of alkalies and water reached in the gels may induce solvent flow into the paste. New alkali fronts may therefore be expected in the inert phase surrounding the moved gel.

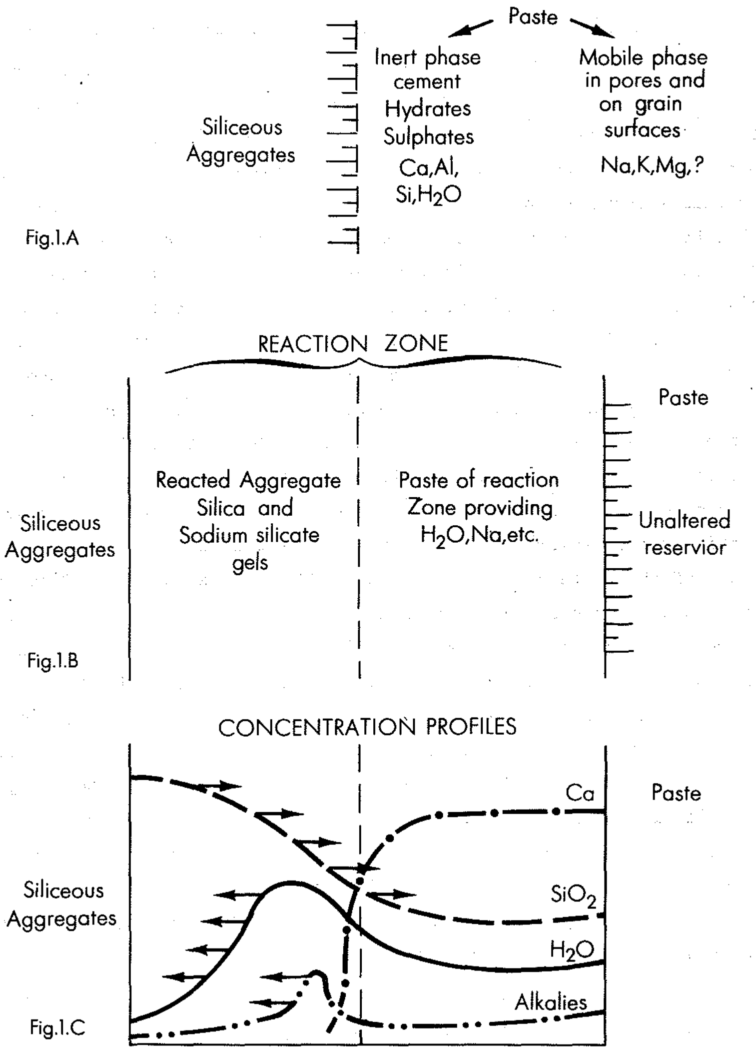

Figure 1. Schematic representation of alkali-silicate reaction in terms of solvent migration. Concentration profiles are given with concentration increasing upwards.

Qualitative Aspects of Solvent Migration in Concrete

Discussion of the application of solvent migration to concretes is facilitated by figure 1. Before reaction commences a simple boundary surface exists between the paste and the aggregate (fig. 1A). The aggregate boundary is represented as a plane and the paste is considered to have the two phases mentioned above. The inert phase includes the growing calcium silicate hydrates and soon acquires all the sulphate and available calcium (7). Considerable space exists between the growing hydrate phases and in this accumulates the residual water. Much of this water is presumably adsorbed onto the surfaces of solids and is dispersed through gels. It is evident that the alkalies are concentrated into this phase (7) though much of the alkali content may itself be adsorbed with the water on the surfaces of the crystallites. For this reason it may be quite difficult to determine the position of these elements even with the electron-microprobe. It is also likely that much of the movement of these soluble ions occurs in this surface layer. All elements must be distributed between the two phases of the paste and distribution coefficients should be definable for each ion and for each in the presence of the others. The data available at present does not allow these coefficients to be calculated but it is evident that Si, Al and Ca are overwhelmingly concentrated into the inert phase for much of the time during which the alkali-silicate reaction takes place. Conversely, Na, K, Li and perhaps Mg are dominantly in the mobile phase. The situation of Fe may vary considerably according to the pH and the oxidation potential of the system and in relatively reducing conditions it is likely that the Fe will enter the mobile phase. Inter-elemental effects may change the equilibria of even the alkalies and calcium and it is likely for example that high chloride concentrations may influence cation distribution coefficients.

After a period measureable in days, months or even years, the planar initial boundary between the aggregate and paste is replaced by a zone of reaction which includes some of the aggregate and that part of the paste that has contributed material to the reaction. The latter may not be noticeably changed except close to the aggregate, for water and ions that have moved into the aggregate may be made up by transfer from the much larger reservoir of paste surrounding the reaction zone (fig. 1B). The concentration gradients to be expected in a simple model involving solvent migration are illustrated in fig. 1C. The direction of motion of the atomic and molecular species are indicated by arrows. Silica diffuses from the aggregate against the aqueous flow and may be expected to show a gaussian concentration profile slightly modified by the influence of the flowing aqueous phase. If Si were to be released from the inert into the fluid phase in abundance at any stage during the reaction it is likely that a silicon-rich band would be produced farther from the aggregate surface. The movement of the silicon away from the aggregate is here presumed to cause the aqueous flow and water will therefore show a concentration profile with a maximum within the zone of reaction. Solutes such as Na and K are concentrated into narrow bands of gaussian form at some position along the path through which flow has taken place. The precise position and form of these bands depends on the relevant distribution coefficients, the forms of the adsorption isotherms and the total amount of each element and uncombined water available. The curves given in fig. 1C are similar to those found in experimental concretes but it is to be expected that gel mobility, particularly in real concretes will distort the concentration gradients considerably. A further complication is that there is little information available concerning the rates of flow of the aqueous fluid. It is to be expected that this must be very slow indeed, a condition that will lead to the formation of sharp concentration bands and hence very high localised concentrations. However, if the rate of motion changes with time or the flow rate varies with direction, the form and position of the migrating fronts will be complicated and lead to lateral discontinuities in concentration.

Quantification of Solvent Migration

If it can be assumed that the adsorption isotherm for the inert and mobile phases of the paste is linear then relatively simple formulae describe the form of the distribution of ions in the flowing fluid. Thus if the distribution coefficient for component 'i' between the two phases is K_i then

$$K_i = C_i^B / C_i^A$$

where C^B and C^A are the concentrations of component 'i' in the mobile and inert phases respectively. If the mass of 'i' in the mobile and inert phases initially are m_i^m and V_i^s and V^m and V^s are the volumes of the mobile and inert phases then

$$K_i = (m_i^m/V^m)/(m_i^s/V^s) \quad \text{and} \quad K_i V^m/V^s = m_i^m/m_i^s$$

If the ratio of the volumes of inert and mobile phases are fixed then m_i^m/m_i^s is a constant which is here termed 'r'. If the mobile phase is allowed to flow through a distance of N units of length then, the $(n+1)^{th}$ unit of length will contain the fraction

$$(N!r^n)/(n!(N-n)!(1+r)^N) \qquad ..1$$

of the total mass of a given mobile element (8). If this mass in the $(n+1)^{th}$ unit is 'w' then

$$\log w = \log N! - \log (N-n)! - \log n! + n \log r - N \log (1+r) \qquad ..2$$

This expression can be differentiated for constant total mass of component 'i' and constant N and r to give the number of units of length from the origin for which the concentration is a maximum. If this maximum is the $(R+1)^{th}$ unit of length then

$$R = Nr/(1+r) \qquad ..3$$

The ratio of the distance moved by the solute to the distance moved by the solvent is then 'R_f' where,

$$R_f = r/(1+r) = n/N = n.h.a/V^m \qquad ..4$$

where h is the unit of length and V^m is the total volume of fluid to have passed through an area of cross section a. The whole form of the distribution of an element can be obtained from these expressions but the width of the concentration band can be more simply found from the empirical formula

$$N = 16n^2/w^2 \qquad ..5$$

where w is the width of the band and n the number of length units at which maximum concentration occurs.

If the form of the adsorption isotherm is not linear the form of the solute-rich band may be changed considerably (5). Also since the R_f value is dependent on K_i then the position of maximum concentration will change if K_i changes. However, from 4 it is evident that a very considerable change in K_i is required to cause substantial difference in the position of this maximum.

Application to an Alkali-Silicate Reaction System

The data required to calculate the form of the solvent migration fronts are not yet available for the concrete system. There is information on the concentration of alkalies in the aqueous paste of the set paste (7) but the amount of water in mobile phase is not known and hence the distribution coefficient for the alkalies cannot be found. However if arbitary values are assumed for the ratio of masses of mobile to inert phases and a fixed value of 0.7M is assumed (10) for the concentration of alkalies in the mobile phase and 0.1M for the whole cement system then K_i can be found for various mass ratios m^m/m^i. Possible values of 'r' can then be plotted against the mass ratio if estimations are made of the densities of the mobile and inert phases (fig. 2A). This graph shows the way in which r approaches infinity as the mass ratio of the two phases increases; reflecting the condition that all the alkali is then in the mobile phase. Values of R_f are then plotted against m^m/m^i in fig. 2B which shows that $m^m/m^i = k(R_f^2 + 2R_f)$ where k is a constant. It is evident that as the fraction of the mobile phase increases so the solute front approaches the solvent front, and the position at which high alkali concentration is attained in the area of reaction is dependent on the proportion of excess water in the mix. With high levels of excess water the alkalies will become concentrated close to the aqueous front while with low levels of surplus water, and hence R_f, the alkali front will be more likely to remain in the paste and outside the area of potential gel formation. With little or no excess water there will be no flow and the alkalies will remain stationary. The assumptions made for the densities of inert and mobile phases are 2 and 1 respectively but the selection of different values for these densities will not change the form of the curves though the constant for the curve in fig. 2B will change. No attempt has been made to refine these relationships further since it is intended to illustrate only the kind of relationship that might be found in concretes pending the aquisition of more satisfactory data.

Further illustrations of the properties of solvent migration in concretes can be made by treating experimental data, such as the analytical data given by Thaulow and Knudsen (1), to show the possible form of concentration gradients to be expected. From this data the experimental concentration-distance curves have been drawn (fig. 3A). In fig. 3B are given the curves expected from the solvent migration model for the

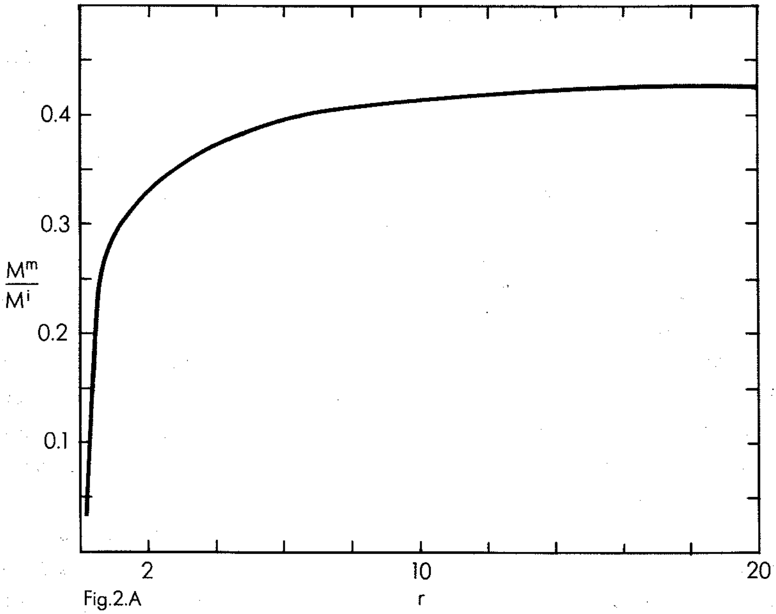
0.4
0.3
$\frac{M^m}{M^i}$
0.2
0.1
2
10
20
r

Fig.2.A

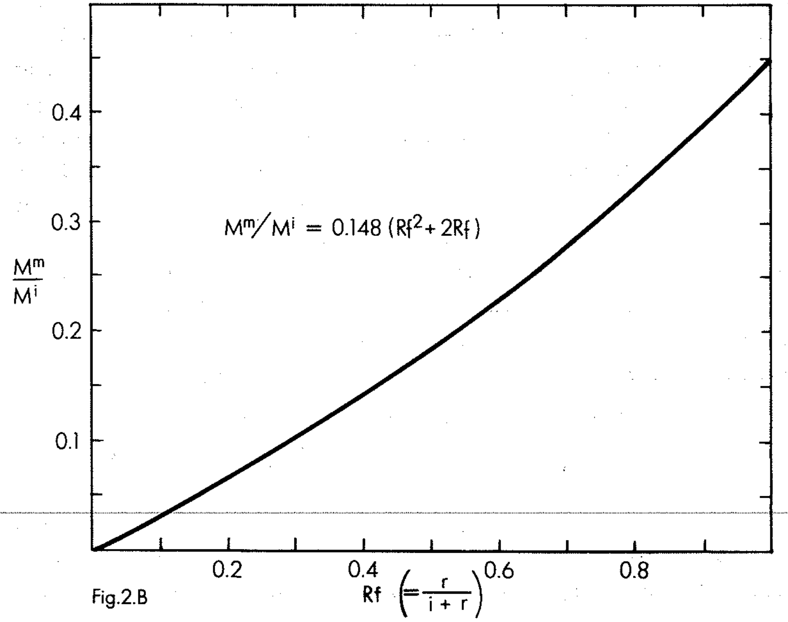
0.4
0.3
$M^m/M^i = 0.148\,(Rf^2 + 2Rf)$
$\frac{M^m}{M^i}$
0.2
0.1
0.2
0.4
0.6
0.8
$Rf\ \left(= \frac{r}{i + r}\right)$

Fig.2.B

width of gel observed experimentally and the quantity of water found to be transferred into the reaction zone. It is reasonable to assume that all the water now in the gel has been transferred from the paste and hence, given an estimate of the volume percentage of mobile phase in the paste, the width of the paste zone required to provide the necessary water can be estimated. Here, the volume fraction of the mobile phase can be estimated at about 0.33 and the total volume fraction of water in the gel zone is about 0.3. This means that since the gel width is about 150µm then the width of paste required to supply the water was about 135µm and the total width of the reaction zone was about 285µm. The effective

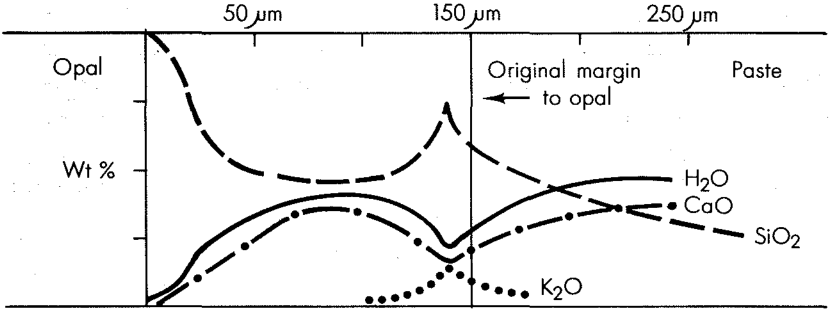

Fig.3.A

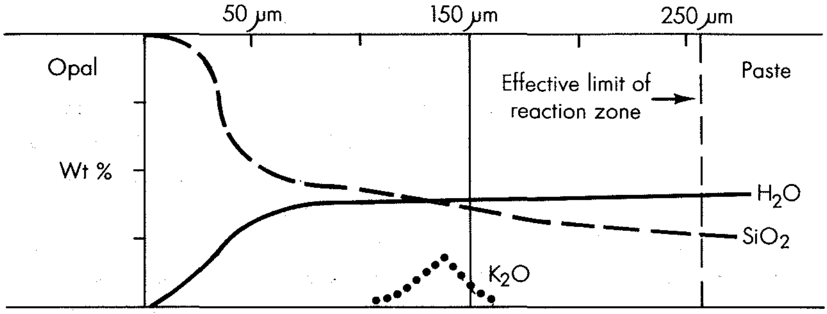

Fig.3.B

Figure 2 (left). Illustrative plots of the variation of 'r' and 'R_f' with the ratio of the mass of the mobile phase to the inert.
Figure 3 (above). Comparison between experimental and calculated (B) concentration gradients in alkali-silicate reaction.

distance travelled by the water front is however best set by considering the maximum in the water concentration-distance curve. This is expected to be about midway through the gel zone. Hence the total effective length of flow may have been about 210µm. With an assumed value of m^m/m^i of about 0.26, corresponding with the estimated volume percentage of the mobile phase, the R_f value would have been about 0.7 and the distance of the alkali concentration maximum from the effective starting surface in the paste would be about 145µm and from equation 5 the width of the band would have been about 40µm.

The exploration of approximations can be taken further by applying the full expression given above (equation 2) to find the concentration levels of the alkalies to be expected in the gel zone. The mobile fluid will have initially about 2% weight of alkalies (as Na-equivalent), and this will be extracted to a maximum concentration of about 2.7% Na_2O-equivalent by weight in the zone of enrichment in the gel. This compares with the experimental value of 1.8% Na_2O-equivalent and is obviously of the correct order; especially when allowance is made for the considerable kurtosis which the experimental water concentration profile shows in comparison with the estimated. This flattening of the water distribution curve would also be expected to apply to the alkali distribution. The assumptions and approximations used in this analysis are not too unreal for the present experimental system and the resemblance between the estimated and observed alkali concentration curves suggests that the model may deserve further exploration in the light of further data.

Conclusions

It is concluded that since experimental observations indicate that water migrates to the site of alkali-silicate reaction and that the distribution of alkalies is discontinuous, then solvent migration may be considered as a possible mechanism for the transfer of material. Estimations based on the formulae normally taken to describe the effects of solvent migration show sufficiently good agreement with the experimental curves to suggest that the search for further data relating to the distribution of ions between the inert and mobile phases would be justified. It is to be expected that if the process applies to alkali-silicate reactivity it may play a part in other processes. Alkali-carbonate reactivity, for example, may be initiated by flow towards hygroscopic aggregate fragments where the active ingredient may be an expansive clay or a highly porous but slowly permeable carbonate. Perhaps also the transfer of material in iron reinforcement corrosion problems, where iron is deposited on surfaces or in porous aggregate fragments, may also involve solvent migration.

The detailed distribution of elements around alkali-silicate fragments will depend on the shapes of the fragments. Sharp edges and corners will show the most rapid accumulation of gel and the highest concentration of alkalies while concave surfaces would be expected to have narrower reaction rims. The increase in alkali in the reaction zone would enhance the solubility of the silicate aggregate and release of silicon into the reaction zone and thence the quantity of water to migrate towards the reaction zone. A chain reaction can therefore be established which is inhibited only by the growing pressure and the availability of water. The total width of the reaction zone should therefore depend on the quantity of water available and the concentration of alkalies in that aqueous phase.

The motion of the aqueous phase towards the aggregate would be expected to change the equilibria that exist between the mobile and inert phases. The production of a zone in the paste which is rich in alkalies, for example, might well modify the solubility of Ca, Si, Al and Mg in the aqueous phase. The possibility exists that while Mg, say, becomes less soluble with the progress of reaction, Ca, Si and Al may become more soluble. These elements may therefore become mobile and move with the alkali front to enter the zone of reaction. It seems not impossible therefore that the silica of the reaction zone is derived from both the paste and the aggregate. Some of the results obtained by A.B. Poole (personal communication) strongly suggests that this is so and that both Al and Ca can form bands of high concentration near the paste gel interface.

If the process of solvent migration is of importance it should lead to the construction of tests for reactivity. A strong dye for example that is highly soluble in the aqueous phase would be expected to migrate with the water and should show up the movement and allow the rate of flow to be measured. In addition it is apparent that if water flow does control the extent to which reaction takes place then the single most important factor in limiting potential reactivity will be the reduction of excess water to the lowest possible levels. Failing that, it may be possible to prevent migration by the use of additives. Either a highly soluble additive may be used that passivates the aggregate surface or a hygroscopic material may be dispersed throughout the paste. The latter would be equivalent to the addition of a pozzolana and perhaps a suitable additive might be dried sodium silicate.

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Val de la Mare Dam

5. IDENTIFICATION AND TESTING OF POTENTIALLY REACTIVE AGGREGATES

THE IDENTIFICATION OF OPAL AND CHALCEDONY IN ROCKS AND METHODS OF ESTIMATING THE QUANTITIES PRESENT

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ABSTRACT

Opal and chalcedony are alkali-aggregate reactive minerals which when present in aggregates used in concrete may give rise to disruptive expansion. Opal and chalcedony mixtures in a form known as beekite have been found as secondary minerals in a suite of igneous rocks including granites, diorites, acid volcanic rhyolites and ultra mafic mica trapps, as a secondary mineral in a mixed suite of rocks from a gravel and opal as secondary material in limestones.

The quantities of beekite present in concrete cores from a structure and from samples of the aggregate used, have been determined by microscopic techniques using very large thin sections.

It has been shown that for rocks of similar porosities the expansion of concrete can be related to the proportion of opal present; the lower the porosity the greater the expansion. However there may be circumstances when after an increase in expansion with increasing opal content there may be a decrease in expansion with further increases in opal content.

Introduction

The most alkali-aggregate reactive form of silica is opal; chalcedony, which is also pure SiO_2, is less reactive and leads to smaller expansion. Both of these minerals are extremely rare in igneous rocks and are then only present as secondary minerals.

Examples of opal and chalcedony in rocks from concrete structures which showed signs of movement, crazing and gel 'pop-outs' characteristic of alkali-aggregate interaction have been studied. Petrographic examination of the aggregates from the concrete showed them to be a mixture of igneous rocks in two examples, granites, diorites, ultra mafic hyperbyssal mica trapps and devitrified rhyolites being identified and of limestone in the third. Petrographic examinations have also been made on a fourth series of rocks which have not been used as concrete aggregates.

Since the expansion of the concrete may be related to the quantities of the reactive minerals (1), it was necessary to estimate the quantities of opal and chalcedony present. Petrographic microscopic techniques using large thin sections were used for this determination.

Identification of Reactive Minerals in the Aggregate

Pieces of aggregate associated with typical surface gel (Figure 1) were removed from a concrete core from an affected concrete structure and subjected to petrographic examination. Opal and chalcedony mixtures in a form known as beekite were identified. Opal occurs as an isotropic material of low refractive index, n about 1.44. Chalcedony is often associated with the opal, it has a low birefingence about 0.009, refractive index $n\beta$ about 1.537.

Thin sections were also prepared from pieces of the aggregate used in the manufacture of the concrete and opal and chalcedony were identified as being present in the following rock types: granite, diorite, microgranite, brecciated felsite, porphyritic rhyolite and rhyolite. The opal and chalcedony which was always clearly secondary, occurred as vermicular growths (Figure 2), as massive material with globular opal set in clear chalcedony (Figure 3). This form of an intimate mixture of opal and chalcedony has become known as beekite although the name originally referred to a sedimentary chert from the Devonian limestones of Devon.

Quantitative Estimation of Reactive Silica Minerals

Since the expansion of concrete is related to the amount of reactive mineral present some means of quantifying the proportion present in the aggregate is required.

Large thin sections about 30 micrometers thick and about 210 x 100 mm or 150 x 80 mm were prepared from either concrete cores or from a melange of quartered down single sized pieces of aggregate, 4 mm average diameter (Figures 4 and 5 respectively).

These large thin sections were then searched on a low power polarizing microscope magnification x13, for any suspect grains which were then marked. On completion of the search the section was transferred to a normal petrographic microscope and the marked grain examined more closely (Figure 6). If beekite was found then the proportion present in the grain was estimated by area measurement. For this work it is assumed that the area is directly proportional to the volume and that since the densities of the materials are similar the volume is proportional to the weight.

For concrete cores the paste proportion was determined as 20% so that after the area of beekite in the thin section was determined it was adjusted to allow for the paste present.

For the aggregate sample examined, all diorite, the slice contained about 750 grains, average size 16 mm^2.

Using the area proportioning technique of examining large thin sections the proportion of beekite in the core was determined as 0.025% and in the aggregate sample as 0.0035%.

Relationship between Reactive Silica Content of Aggregate and Expansion

The expansion of concrete is related to the amount of alkalies present in the cement, the quantity of reactive silica in the aggregate, the form in which the reactive material is present, ie porosity and the quality of the concrete. Table 1 and Figure 7 give the data on a number of mortar bars made with basalt aggregate containing varying proportions of opal. The opal was from a malmstone with a porosity of 41.5%. The bars were made according to the method of Jones and Tarleton (2) and the cement was made up to contain either 0.7% or 1.2% combined alkalies ($Na_2O + 0.656 K_2O$).

TABLE 1

Expansion at 140 Weeks of Low Quality Mortar Bars made with Aggregate Containing Varying Quantities of Opal

% Opal	Expansion as percentage of length	
	Low alkali cement (0.70%)	High alkali cement (1.2%)
0.25	0.025	0.042
1.25	0.015	0.077
2.5	0.015	0.021
5.0	0.020	0.019

These results show that for the low alkali cement the expansion increases with increasing opal content, but with the high alkali cement the mortar bar expansion increases with increasing opal content up to about 1.25% opal and then decreases as the opal content is further increased.

Jones and Tarleton (2) examined a series of mortar bars using Siliceous magnesium limestone (SML) and Nebraska Gravel (NG) but no attempt was made by them to determine the quantity of opal present in the rocks. Using the techniques of area measurement of thin sections the quantities of opal present in these rocks has been determined and thereby the amount of opal present. The Siliceous magnesium limestone had a porosity of 6% and an opal content of 0.6% and the Nebraska Gravel had a porosity of 3% with an opal content of 0.125%.

Mortar bars were made by Jones and Tarleton using an inert basalt as a diluent and the results of expansion at 1 year when compared with opal content are given in Table 2. The results are plotted together in Figure 8.

TABLE 2

Expansion in Percent of Length of Poor Quality Mortar Bars at 1 Year (Cement contains 1.2 Per Cent Combined Alkalies)

Per Cent Opal	Expansion %
SML	
0.03	0.032
0.15	0.18
0.30	0.42
0.60	0.78
NG	
0.006	0.017
0.013	0.017
0.025	0.022
0.06	0.027

New experiments have also been carried out on granitic rocks, porosity about 3% which were estimated to contain various quantities of beekite. The expansion at 1 year using mortar bars made to the Jones and Tarleton specification are given in Table 3.

TABLE 3

Expansion in Percent of Length of Poor Quality Mortar Bars at 1 Year (Cement contains 1.2 Per Cent Combined Alkalies)

Per Cent Beekite	Expansion %
0.00	0.015
0.004	0.021
0.025	0.03

These have also been plotted as a combined graph in Figure 8.

The effect of porosity of the opal bearing rocks can be seen by comparing the results of the porous malmstone (porosity 41.5%, 0.25% opal, expansion 0.042%) with the results from Siliceous magnesium limestone (porosity 6%, 0.3% opal, expansion 0.42%). The highly porous malmstone had, for a similar quantity of opal only one tenth of the expansion of the less porous limestone. The probable explanation for this is that the sodium silicate gel which is the expansive agent is absorbed in the pores of the highly porous rock and is not available for expansion. For the aggregates of lower porosities, all the results of expansion with similar mortar bars show a similar relationship and may be plotted on one graph, Figure 8.

Conclusions

Opal and chalcedony have been identified as secondary minerals in igneous rocks. The quantities of these minerals may be estimated by area measurement of thin sections of either concrete or aggregate particles.

If the rocks have similar porosities, then the expansion of mortars made with similar cements of high alkali contents will be related to the quantities of reactive silica present.

Acknowledgement

The work described has been carried out as part of the research programme of the Building Research Establishment of the Department of the Environment and this paper is published by permission of the Director.

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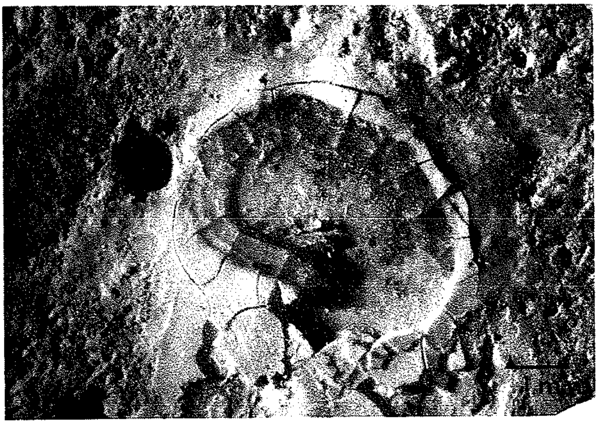

Fig 1 Gel formed on surface of concrete core stored in 100% RH for 1 month.

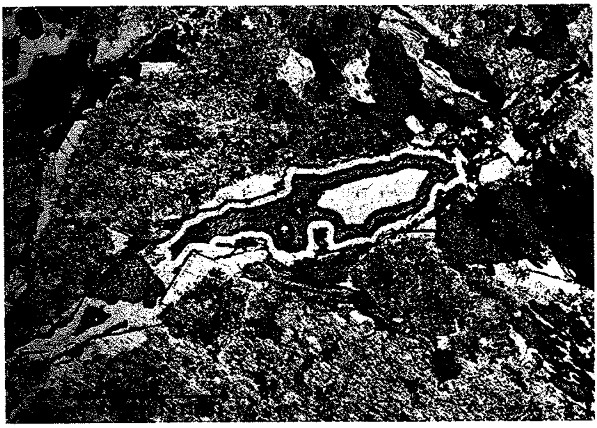

Fig 2 Optical micrograph of vermicular opal and chalcedony in diorite.

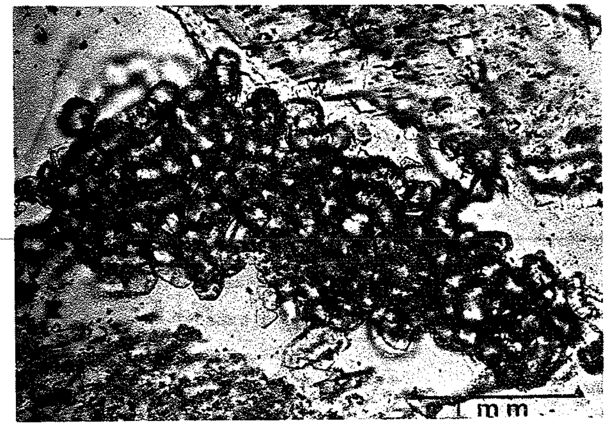

Fig 3 Optical micrograph of globular opal in diorite.

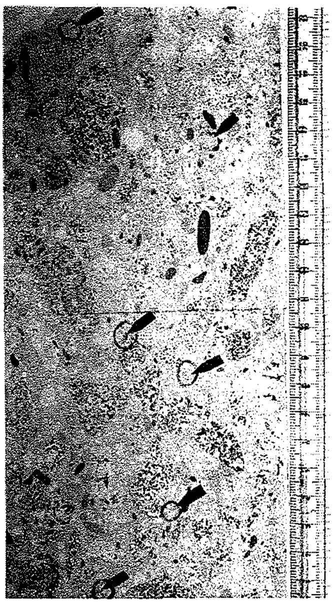

Fig 4 Low power photomicrograph of thin section of concrete core with marked suspect grains.

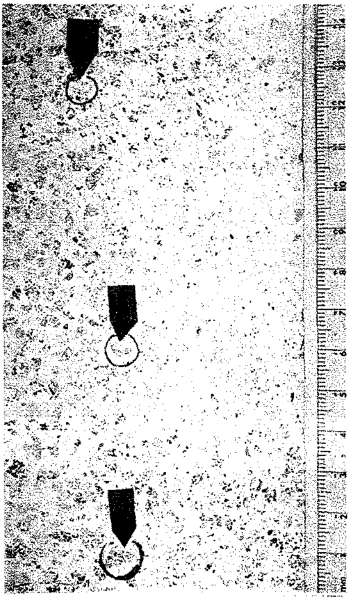

Fig 5 Low power photomicrograph of thin sections of aggregate particles with marked suspect grains.

Fig 6 Optical micrograph of suspect grain from cements core.

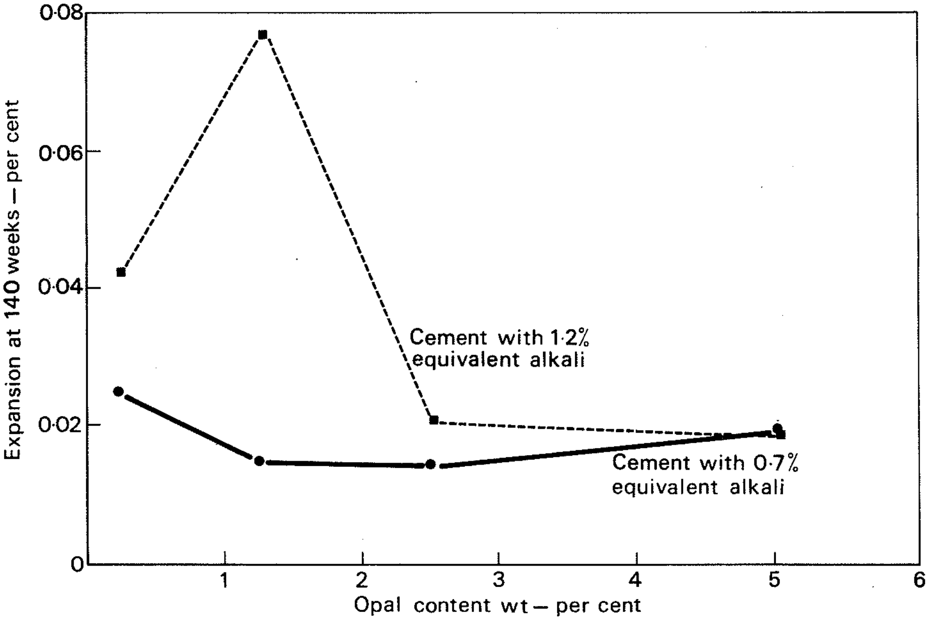

Figure 7 Relationship between opal content of aggregate and expansion at 140 weeks for poor quality mortars, made with cements of different alkali contents

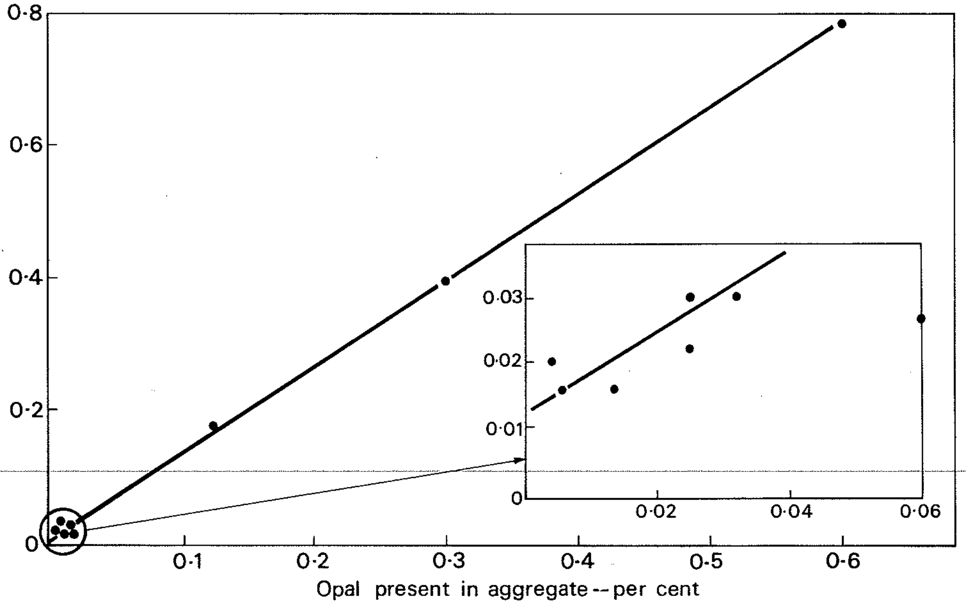

Figure 8 Relationship between opal content of aggregate and expansion at 1 year, for rocks with low porosity

PETROGRAPHIC INVESTIGATION OF ALKALI-REACTIVE SILICATE ROCKS IN SEVERAL STRUCTURES

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ABSTRACT

The identification of potentially reactive aggregates is a very responsible and one of the most difficult task of a petrographer. To establish the alkali reactivity of silicate rocks proves to be especially complicated because of the great number of rocks which may be reactive. Three examples of alkali reactive rocks from deteriorated concrete structures are described. The aggregates are: quartz arenite, quartz wacke and argillaceous quartz wacke, and distinctly deformed dacite. The problems in identifying the reactive varieties of these rocks especially in bulk aggregate samples are emphasized.

Petrographic examination is one of the important techniques for identifying rocks that are potentially alkali reactive when used in portland cement concrete. The petrographic identification of alkali reactive rocks is based on a knowledge of, or direct comparison with, rocks that are proven to be alkali reactive. It is generally recognized that the petrographer cannot predict that a rock will be reactive if there is no previous record of reactivity for that particular type of rock. It is well to understand that a petrographic examination by itself is not an absolute assurance against the inclusion of alkali reactive material in portland cement concrete.

The petrographic identification of alkali reactive rocks and varieties suspected of being alkali reactive is based on examination to determine the composition and texture of rocks and on the identification of the products of alkali-aggregate reactions. For the siliceous reactive rocks, the reaction products are the rims and silica gel which are formed when reactive aggregates are incorporated in concrete. The presence of alkali reactive aggregates in concrete can also be confirmed by identification of physical effects associated with reactivity; the expansion primarily of the aggregates and subsequently of the concrete. The closing of joints, disalignment of structural elements, misalignment of machine sets, cracking of the aggregates and the cement paste, pattern cracking of the concrete surface and general disintegration of the concrete are evidence of the expansion.

This paper is a discussion of the difficulties and uncertainties faced by the petrographer in identifying alkali-reactive silicate rocks or silicate rocks suspected of being alkali reactive. The purpose of emphasizing the problems and difficulties is to encourage further work and perhaps help to point out the direction in which further work and answers are urgently needed.

Methods of "Routine" Petrographic Analysis

The main petrographic method for identifying alkali reactive rocks is by careful examination of the composition and texture of the rocks and by comparing rocks with others that are known to be alkali reactive. The basic guidelines for petrographic examinations are given in the ASTM Designation C295. The new proposed "Standard Recommended Practice for Petrographic Examination of Hardened Concrete" ASTM Designation C (?) provides a method for the examination of aggregates in concrete. Many excellent papers by various authors such as K. and B. Mather (e.g.11) and R. Mielenz (e.g.12) describe detailed petrographic methods applicable to concrete aggregates and concrete. Detailed petrographic examinations of alkali reactive rocks in Canada was made by Gillott, Swenson and Duncan (16, 17, 7).

Difficulties in Identification of Reactive Silicate Aggregates in Concrete

As mentioned, the basis for petrographic identification of reactive aggregates are concrete structures which show distress typical for alkali reactive aggregates: dark rims on crushed aggregate particles are frequently the first features observed, gel as the product of reactivity, characteristic expansion cracks in the reactive particle extending into the cement paste and pattern cracking on the surface of a concrete. In addition, proof of reactivity requires that the aggregate has been used with high alkali cement in a concrete exposed to a moist environment. If these conditions were not fulfilled, an erroneous conclusion could be made that an aggregate is not reactive. Although cracking and reactive expansion are typical signs of reactivity, similar cracking may be caused by other factors such as freezing and thawing.

When examining single aggregate particles, the weathering rims that occur in natural sands and gravels may be mistaken for the secondary dark rims that are a positive indication of alkali-aggregate reaction. If both gravel and crushed rock have been used together in a concrete, then it is necessary to examine the rims on crushed particles only.

The presence of silica gel is usually considered to be the best proof that alkali-silica reactive aggregate is present in a concrete. Difficulty in detecting and identifying silica gel may occur for various reasons such as (a) unsatisfactory sampling of the concrete, (b) the silica gel may be partially crystallized and complex due to repeated gel formation, (c) it may be "contaminated" with various oxides and therefore may not have the same appearance as the classical isotropic gel, (d) it may be coated with other products, (e) it may be leached out. In thin sections, gel may be lost during the preparation of the thin section if insufficient care has been taken to preserve it.

Incorrect sampling may cause difficulty in determining the most reactive rock or variety in an aggregate; this applies especially for multilithic aggregates. It is frequently difficult to establish which particle originated the gel on the surface of a crack. Secondary products such as calcite or ettringite or both, which may also be developed on cracks opened and enlarged by reactive aggregates, may cover the silica gel. Calcite may be present as a crust on the gel, as small prisms or as minute rhombohedrons. Ettringite may be present as long fibres indicating that it developed in a fairly open crack. Gel is not always easily identifiable and many mounted sections of the secondary products may have to be examined to make an appropriate judgement about the extent of alkali reactivity.

Examples of Alkali Reactive Silicate Rocks in Concrete

Silicate rocks which are alkali reactive may occur in various compositional or textural varieties or both. Precise determination of the variety of a rock that is reactive is often difficult because it has been proven that for most rocks, similar or petrographically equal varieties may be either innocuous or reactive to varying degrees. This has been experienced with silicate rocks from the Canadian Shield (5) and it can be assumed that it applies to varieties of sandstones and an acid volcanic rock which were examined recently. These rocks were used as aggregates in large concrete structures which required repeated extensive repair. Parts of the structures showed pattern cracking varying in intensity at different locations. Distinct cracking parallel to the edges and outer surfaces indicated deterioration due to frost action. The concrete in each structure contained gel and additional secondary products consisting of abundant calcite and various amounts of ettringite. The three aggregates are described in the following detail.

Example 1

Coarse and fine aggregates consist of quartz arenite (orthoquartzite), very subordinate calcitic quartz wacke and some blending sand (?).

Concrete containing these aggregates was used in a lift bridge, in a hydraulic lock and in a hydro-electric generating station. Of the three aggregates discussed in this paper, this aggregate causes the greatest problems. Disalignment necessitates repeated repair. The concrete shows pattern cracking, in some areas with a well developed large pattern of wider cracks enclosing a smaller pattern with narrower cracks.

Example 1: Quartz Arenite

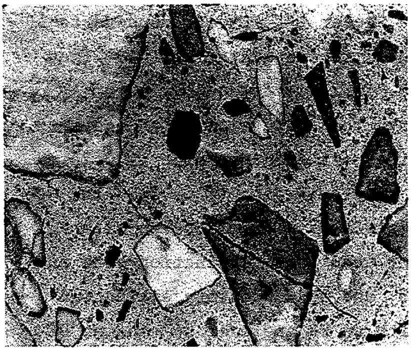


FIG. 1

Cracked coarse, fine aggregates and cement past (1.1x)

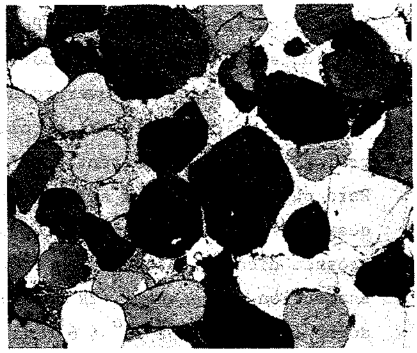


FIG. 2

Quartz wacke with calcitic cement (65x), T.S. crossed nicols

FIG. 3

Quartz arenite with fine-grained quartz and clay interstices (62x), T.S. crossed nicols

FIG. 4

Cracked quartz grains in arenite (65x), T.S. crossed nicols

Figure 1 shows the coarse and fine aggregate particles in the concrete with cracks crossing the aggregates and extending along the aggregate-cement paste paste interfaces into the cement paste. The aggregate rock is whitish to greyish, less frequently slightly brownish. A narrow rim (0.3 mm in the average), usually one or two quartz grains deep, is developed in most particles. The border of the rim toward the inside of the aggreate is gradational. Gel occurs in cracks but is lost during thin section preparation.

The aggregate is a uniform quartz arenite according to the classification by Pettijohn, Potter and Siever (14), with rounded to subrounded, well sorted to moderately well sorted quartz grains. They are mostly cemented by overgrown silica, far less frequently with secondary calcite (FIG. 2) or clayey material. The size of the quartz grains varies in different particles, the most frequent size is 0.25 mm. Rare particles contain stripes of much smaller grains (FIG. 3). The quartz grains are usually homogeneous (see FIG. 2 and 3 taken with crossed nicols). Few grains show slight undulatory extinction with an extinction range angle (ER angle) of 13° and an undulatory extinction angle (UE angle) of 30° (6); grains with an ER angle of 26° and an UE angle of 53° are exceptions. Cracking of larger quartz grains is frequent in some areas (FIG. 4) but few are broken into smaller pieces or are separated into small grains by the calcite cement.

In general petrographic terms, the rock is uniform as are most of the quartz grains. Based on the composition and texture one would not predict this to be a highly expansive rock. The border lines between the original quartz grains and the later growth indicates that lattice irregularities may occur there. Calcite indentations into the quartz grains occur along portions of the interface between the cementing calcite and many quartz grains.

About 20 years ago, petrographic examinations were done on samples of crushed coarse aggregate and manufactured sand, obtained from a quarry which supplied aggregate for a portion of the structures. Megascopic and microscopic examinations showed that the aggregates were of the same kind as those in the concrete examined recently. The quartz arenite consisted mostly of fine to medium quartz grains and a few varieties contained layers rich in coarse sand. The cement, 10 to 20 percent, was formed by secondary overgrowth of quartz, in patches it was calcitic or consisted of clayey material. In 25 thin sections used in the previous and recent examinations, the clayey material did not amount to 5 percent of the rock by estimation. The carbonates amounted to 1.1 percent in the fractions of manufactured sand indicating that calcitic cement was rare. At this time, the alkali reactivity of the rock was not recognized and there was no obvious cracking in the concrete which, at that time, was about 20 years old. This would indicate that the quartz arenite belongs to the group of slow expanders.

Example 2

The coarse concrete aggregate consists of crushed sandstones grading to siltstone and shale or orthoquartzite.and gravel consisting predominately of these rocks and subordinately carbonate rocks. The fine aggregate is a natural sand of the same composition as the gravel with monomineral grains prevailing in the finer fractions.

Example 2: Sandstones

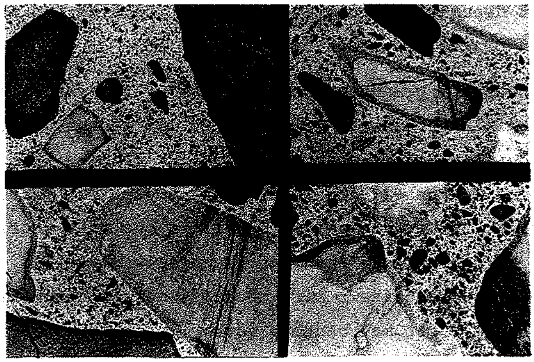


FIG. 5

Red argillaceous wacke and greenish quartz wacke both with rims and cracks (0.94x) 0,64

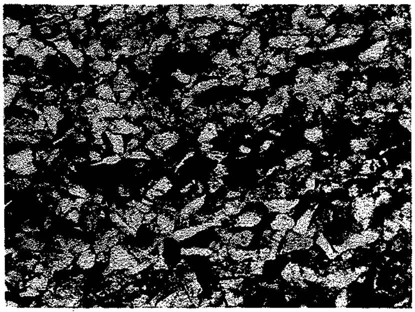


FIG. 6

Argillaceous wacke with dark argillaceous concentrations showing crack (65x) T.S. crossed nicols

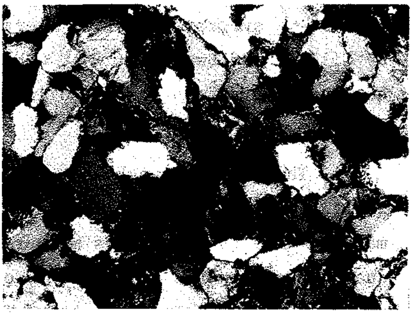


FIG. 7

Quartz wacke grading to arenite with mica scales at quartz borders (65x) T.S. crossed nicols

The 40 year old concrete used in hydraulic locks and bridges show extensive cracking, scaling and spalling and typical pattern cracking in some locations. Many coarse aggregate and several particles of the coarse sand fraction show dark rims measuring 1 to 4 mm. in width with little variation in a given particle (FIG. 5).

Secondary products are very abundant in the outer areas of the concrete but decrease toward the inner ends of the 3 to 8 foot long drill cores which were examined in detail. The products consist of silica gel and abundant deposits of relatively compact calcite and fluffy ettringite developed in cracks and voids.

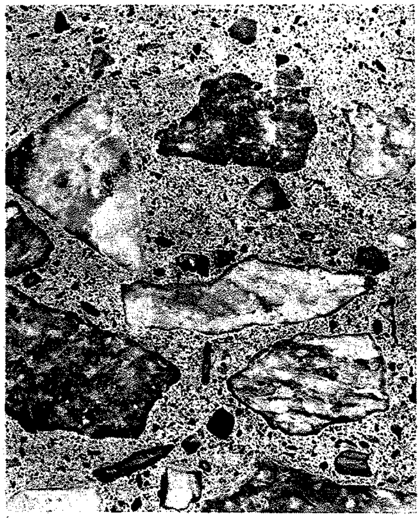
The coarse aggregate consists mainly of two varieties of sandstones, a reddish argillaceous wacke grading into siltstones and even shales and a somewhat less frequent greenish quartz wacke grading into quartz arenite, Both varieties may be developed in the same concrete particle. The reddish wacke is usually finer grained (0.07 mm. in one thin section), the grains are angular to subangular, than the greenish wackes (FIG. 6 and 7). The reddish rock also contains a more abundant matrix consisting of hematite and clay minerals. It may contain narrow layers richer in the clayey matrix or even small argillaceous lenses. Particles of the reddish distinctly argillaceous sandstone and especially the argillaceous lenses are prone to cracking parallel to the layering (see FIG. 6). The rims and gel deposits along the rims in the wacke show that the variety is definitely reactive. Although no data of the exact amount of clay-grade constituents are available, the rock seems to have some similarity to the alkali reactive subgraywacke from Alert, Elleswere Island, examined in detail by Gillott and Swenson (8). The presence of gel in this rock seems however to indicate that also in this wacke quartz is involved in the reaction.

The greenish wacke consists of angular to subrounded uniform quartz grains, much less abundant feldspar grains and a scarce clayey matrix. The quartz grains measure about 0.20 mm. in size and show frequent quartz overgrowth. This variety of the sandstones with some similarity to quartz arenites is also reactive forming reaction rims with gel deposits.

Example 3

Coarse aggregate crushed distinctly deformed dacite. Fine aggregate natural sand with fragments of the crushed volcanic rock in the

Example 3: Distinctly Deformed Dacite



0.68X

FIG. 8

Segregation of cracked aggregates and cement paste. Life size.

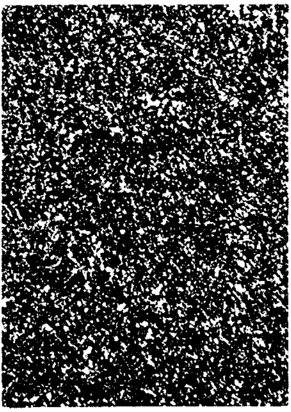


FIG. 9

Uniform cryptocrystalline groundmass (65x). T.S. crossed nicols.

FIG. 10

Uniform plagioclase and strained quartz in fine grained groundmass (35x) T.S. crossed nicols.

FIG. 11

Branching crack with gel and desiccating cracks in microcrystalline groundmass (78x) T.S. polar. light.

coarse "sand" fractions.

The concrete is used in a bridge which shows distinct cracking in the piers and typical pattern cracking in the sidewalks. The coarse aggregate particles showed narrow rims, 0.1 to 0.9 mm. in thickness (FIG. 8). Gel and calcite deposits were abundant on cracks and in air voids in some concrete pieces but were scarce in other pieces that were available for examination.

The coarse particles are very heterogeneous but consist of one rock type only which is a dacite with well developed large phenocrysts twinned plagioclase (subordinate potash feldspars) and quartz.

The groundmass consists of quartz, feldspar, mica and locally of chlorite scales. The micas are aligned in some areas giving the rock a slightly schistose appearance. The size of the constituents varies greatly. It is most frequently microcrystalline, in small areas homogeneous cryptocrystalline, with an average grain size less than 0.01 mm. (FIG. 9), in other areas it is fine crystalline.

The most characteristic feature of the rock is the distinct deformation, which increases its heterogeneity. It is least evident in the feldspar phenocrysts which show a patchy extinction or they are broken into several pieces. The cracks do not always follow cleavage planes. Quartz phenocrysts show a distinct wavy extinction (FIG. 10) and cracks separating them into smaller grains. The average ER angle is 7° and the UE angle 30°. Shearing planes and microfolding are visible in the groundmass. Lenses and accumulations of muscovite scales represent what seems to be former mafics. Aggregations of quartz coarser than the groundmass are developed in the shadows of the feldspar and quartz phenocrysts. Some quartz may have been introduced later as were pyrite grains which are disseminated in some particles. Calcite occurs in rare patches. Distinct cracks are developed in the concrete aggregates. They follow the mica rows but also cross the groundmass irregularly. In two thin sections gel was preserved in the cracks, in both instances in areas of the groundmass (FIG. 11).

Unsolved Problems

Detailed examination with the petrographic microscope and some x-ray analysis left many pertinent questions unanswered. Rims were not easily detectable under the petrographic microscope. Normal optical methods did not show identifiable signs of reaction such as surface indentation on medium or coarse quartz grains. In the quartz arenite, it could not be determined if only the small quartz grains and the portions of quartz overgrowth were alkali reactive or if the medium and coarse quartz grains were also reactive. It is hard not to assume the latter, although signs of lattice disturbance were rare and no imperfections were evident. It was not determined whether the rare calcitic quartz wacke varieties were reactive. Alkali reactive quartzites (quartz arenites) involving coarsely crystalline quartz have been reported from other areas (3 , 7).

In the second example of wackes and arenite, it could not be determined if the quartz grains or the matrix are reactive or both. The amount of argillaceous material that must be present in sandstones (wackes) and siltstones to make them unreactive was not determined. The silty shales present in the concrete areas where gel occurred on sandstones showed only cracks parallel to the fissility and no development of gel although the silt grains were apparently minute quartz grains.

The distinctly deformed and devitrified dacite presents special problems. It is known that a devitrified groundmass of acid volcanics is alkali reactive. Cracks in the cryptocrystalline (grain size less than 0.01 mm (13)) and microcrystalline groundmass are filled with gel. Some cracks occur within mica-rich lenses but traverse the mica lineation in areas with fewer micas. This rock is secondarily altered but judging from the presence of cracks and gel the alteration has not significantly diminished the reaction, if it has influenced it at all. The extent to which this would apply to other rocks is not known.

Some of these questions might be answered by modern scanning electron methods which provide micrographs (16,8) and by x-ray element distribution photographs (19). The former is more and more widely used in investigations of alkali reactive aggregates.

Examination of Rock Specimens and Bulk Aggregate Samples

It is much easier to determine the reactive silicate rocks in concrete petrographically than to assess the potential reactivity of an outcrop or a quarry. It is even more difficult to determine the reactivity of bulk aggregate samples from multilithic pits. An exceptionally large number of particles would have to be examined in thin sections or mounted powder sections to establish reactivity if only about 2 percent of the rocks were reactive. Some rocks cause deterioration of concrete at this concentration.

Far too little experience is yet available to identify in bulk aggregate samples reactive granitic rocks, charnokites and granite gneisses (19,9) a few of which are described as being alkali reactive although strained quartz may give some indication (18,6). It would be unjustifiable to classify all granitic rocks and granitic gneisses as suspected of being alkali reactive on the basis of the few reported alkali reactive examples when the same rocks have been widely used in concrete without causing distress. The examples from India indicate that the concrete was exposed to higher temperatures than are normal in moderate climates.

It has to be repeated that without examination of concrete structures containing similar aggregate and/or adequate laboratory tests petrographic examinations cannot establish whether an aggregate without a service record is potentially alkali reactive. Concrete structures made with an aggregate which can be identified with sufficient degree of exactness must be available. There are newly developed areas in which no concrete structures are yet built. The same or identical rocks submitted for petrographic examination have to be tested for expansion before it can be concluded that the aggregate source contains potentially reactive material. The examination of expansion in rock cylinders ASTM C586 gives an important clue to which varieties are expansive. The test of rocks in easily prepared small prisms (1-1/8" by 1/8" by 1/4" or approximately 30 x 3 x 6 mm) proposed by Grattan-Bellew and Litvan (10) is promissing. Relatively small gravel pieces could be tested.

General Petrographic Questions Regarding Alkali Reactive Silicate Rocks

There are many basic questions of general petrographic interest which cannot be resolved using the normal methods and equipment available to a petrographer. The main problems are connected with medium to coarse grained quartz-rich rocks. It has to be assumed that minute quartz grains are probably developed on the surfaces of larger quartz grains, in interstices, along channel ways into which alkali solutions can penetrate, and on microcracks. Are these minute quartz grains causing alkali reactions or it is correct to assume that even coarse quartz grains are alkali reactive? What is the role of an argillaceous matrix containing quartz in silt or clay size? In these cases, are the amounts too low to influence the degree of reactivity of the main constituent of a silicate or carbonate rock? Should it be assumed that quartz is the most important and abundant constituent in devitrified volcanic glass? How coarse must be the groundmass in an acid porphyritic rock, a type of felsite, to prevent it from being reactive? How does metamorphic alteration influence volcanics? What is the influence of chalcedonic chert inclusions on the reactivity of carbonate rocks? These are some of the questions connected with the aggregate rocks discussed in this paper.

Conclusion

The petrographer when examining concrete aggregates for alkali reactivity deals with two different problems:

1) to determine whether a concrete is prematurely deteriorated because it contains alkali reactive aggregates and

2) to determine whether an aggregate source is potentially alkali reactive.

Detailed examination of deteriorated concrete containing alkali reactive aggregates helps to become better acquainted with some varieties of the numerous silicate rocks which are alkali reactive.

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Mr. D. St.John

My experience has been similar in that while I have seen reaction rims around aggregates in fracture surface I have not always been able to see the same rims in thin section. In one particular case, of a pyroxene andesite which consisted of more than 60% reactive glass, I considered that such a large area of surface was available for reaction that at any one point on the surface of the aggregate reaction had not proceeded to the point where it was visible in thin section.

Mrs. K. Mather

Evidence of alkali silica reaction is sometimes visible only as rims on crushed stone and as "main cracks" as described by Gunnar Idorn and excellently illustrated in two diagrams in his book. These illustrations are of great value to all petrographers.

Dr. P. Grattan-Bellew

I would like to add further comments to the discussion by K. Mather on the problem of observing gel in sections and polished slabs, etc., the point was made that during the course of time gel may get washed out. My comment is that gel may get washed out as one tests a gel extracted from concrete made with reactive aggregate and high alkali cement have shown. At least 50% of the gel is readily soluble in water, the bulk of the remainder being soluble in dilute HCl.

ALKALI REACTION TESTS
WITH SOUND AGGREGATE

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ABSTRACT

Sound aggregates like sand and gravel of quartz without flint or opaline material have never been the cause of any trouble in normal concrete structures in Germany even if cements with high alkali contents were involved. On the other hand, this does not necessarily have to mean that each sound aggregate cannot react with the alkalies of the pore solution. Several experts have already indicated that nearly all aggregates can react, at least under extreme experimental conditions.

This phenomenon was investigated applying mortar tests with normal sound quartz aggregate. The extreme conditions were: High cement content, low w/c ratio, very high humidity, and a temperature of 40 °C. 13 cements with alkali contents from 0,5 to 1,2 wt % were tested over a period of 12 months.

The expansions of low alkali cements were very much lower than in Pyrex mortarbar tests. Portland cements with $\leqq$ 0,6 % alkali (Na_2O-equivalents) caused only expansions < 0,4 mm/m, Portland cements with > 1,0 % alkali, however, produced expansions > 1 mm/m. All the expansions of the slag cements with > 40 % slag were < 0,4 mm/m. The influence of the granulated slag was very nearly the same as in Pyrex mortarbar tests.

Introduction

It is a wellknown and fully accepted experience that in Germany destructive alkali silica reaction never occured in normal concrete structures if low alkali cements (PZ-NA or HOZ-NA) had been used or if the aggregate contained only sand and gravel of quartz without reactive flint and without opaline material (1).

On the other hand, it is also wellknown that in laboratory tests the expansion of low alkali cements can easily go up to 1,5 mm/m if pyrex glas aggregate is applied (2). Regarding the reactivity of different natural aggregates several experts have already indicated that almost all aggregates can react, at least under extreme experimental conditions (4,5,6).

For better understanding of these phenomena all the other parameters which are necessary for alkali silica reaktion or which increase its effect have to be taken into consideration, i. e. high relative humidity, elevated temperature, high cement content, low w/c ratio, pessimum grading of the aggregate.

The purpose of many laboratory investigations and especially of mortarbar tests is very often only to classify a cement, an additive, or an aggregate. In these cases all the remaining parameters are usually applied in extreme combinations which can never occur in a concrete structure - at least not in Germany. Under such very special experimental conditions even low alkali cements can expand distinctly with reactive aggregates, or high alkali cements can react with aggregates otherwise known as sound. That way it is even possible to force clean quartz aggregate to a weak but measurable alkali aggregate reaction.

Experimental Procedure

The expansion of mortarbars 4 x 4 x 16 cm with steel gage studs on each end was measured monthly over a period of 12 months. The prisms were demoulded after one day and then stored in closed moist boxes ($>$ 95 % RH) at 40 ^{o}C. The reference length of the prisms was measured after three days $(\Delta = 0)$.

The mix proportion in % by weight was

water/cement/aggregate = 0,43/1/2,25

i.e. a cement content of 600 kg/m^3. The aggregate grading was

mm	0/0,2	0,2/1	1/3	3/7	7/15
wt-%	10	30	20	20	20

The aggregate consisted of normal sound quartz material which passed the petrographic examination (ASTM C 295) and the quick chemical test (ASTM C 289) as nonreactive. 13 cements with contents of granulated blastfurnace slag from 0 to 70 wt-% and with alkali contents (Na_2O-equivalents) between 0,5 and 1,2 wt-% were tested.

Test Results

The characteristic cement data and the expansion test results after 12 months are given in Tab. 1.

TABLE 1

Results of Mortarbar-Expansion-Tests

N$^{\underline{o}}$ of cement	blastfurnace-slag in wt-%	Na_2O-equivalents in wt-%	expansion in mm/m
1	0	1,20	1,66
2	0	1,11	1,19
3	0	0,48	0,21
4	13,0	1,12	0,94
5	39.0	1,08	0,47
6	41,3	0,84	0,24
7	47,6	0,78	0,23
8	48,2	0,99	0,32
9	49,0	1,08	0,31
10	59,0	1,08	0,21
11	65,3	1,06	0,21
12	68,5	0,75	0,20
13	69,5	0,87	0,15

This table shows distinct expansions up to more than 1 mm/m even though only quartz aggregate had been used. Moreover it provides another proof of the wellknown experience that blastfurnace slag in cements reduces the reaction to very low degrees even if the alkali content of the blastfurnace slag cement exceeds 1 wt-% (3,7,8).

The quantitative statistical evaluation of the results received in this special experiment leads to the formula

$$\Delta_Q = 0{,}826 \cdot \left[A \cdot (1 - {}^{H}/_{100}) \right]^3 + 0{,}165 \qquad (1)$$

Δ_Q: expansion after 12 months in mm/m

A : Na_2O-equivalents in wt-%

H : content of granulated blastfurnace slag of the cements in wt-%

The coefficient of correlation of equ. (1) is $r^2 = 99{,}0$ %. That means that an exact calculation of the influences of alkali and blastfurnace slag is possible. Tab. 2 shows the results of this calculation

TABLE 2

Calculated Expansion of Mortarbars with Quartz Aggregate in mm/m

Na_2O-equivalent (A) in wt-%	content of granulated slag (H) in wt-%			
	0	25	50	75
0,0	0,17	0,17	0,17	0,17
0,3	0,19	0,17	0,17	0,17
0,6	0,34	0,24	0,19	0,17
0,9	0,77	0,42	0,24	0,17
1,2	1,59	0,77	0,34	0,19
1,5	2,95	1,34	0,51	0,21

Tab. 2 is valid only for this special mortarbar experiment. It is likely that the term + 0,165 mm/m in equ. (1) is only an experimental constant which is not due to alkali silica reaction. That would mean that all the calculated values of Tab. 2 should be diminuished by 0,17mm/m if the alkali reaction only shall be taken into consideration. In this case low alkali cements would create alkali expansions of $\leqq$ 0,2 mm/m and high alkali cements would produce alkali expansions up to more than 1 mm/m under these experimental conditions.

In any case the influence of the granulated slag is very nearly the same as in pyrex mortarbar tests: Blastfurnace slag cements with 50 wt-% slag and 1,2 wt-% alkali react like portland cements with 0,6 wt-% alkali, and blastfurnace slag cements with 75 wt-% slag create little if any expansion.

Conclusion

If the experimental conditions of accelerated laboratory tests are powerful and sophisticated enough, it is likely that almost all SiO_2 containing aggregates can be forced to a reaction with concentrated alkali solutions even those which would never be harmfull to a concrete. When such laboratory tests are applied, it is therefore necessary to compare the results of an unknown material with the results of a familiar reference material that was tested exactly the same way. As far as the northern part of Europe is concerned a comprehensive research work on natural aggregates has been done in Denmark and in Germany (1,9) and the difference between harmful and innocuous material of this area is wellknown. After all, if the unknown aggregate behaves like quartz it cannot possibly be classified as deleterious.

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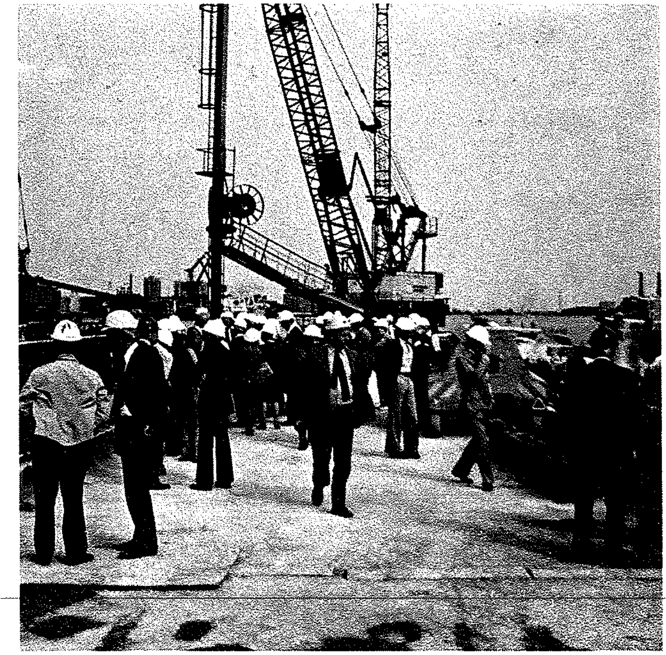
Dr. P. Grattan-Bellew

The point that almost all aggregates can be made to expand under accelerated laboratory test conditions, stated by Dr. Smokzyk, is well made. Under such laboratory conditions it is essential to run parallel tests on reference aggregates with known expansion characteristics in concrete, so that "accelerated normal expansions" are not misinterpreted as being deleterious.

Mrs. K. Mather

I would suggest to Dr. Gratton-Bellew that a fine grained pure dense limestone is a good control aggregate for alkali-silica reaction mortar bars.



The Thames Barrage Site

TESTING CANADIAN AGGREGATES FOR ALKALI EXPANSIVITY

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ABSTRACT

The applications of the chemical test ASTM C289, the mortar bar test C227, a modification of it, the rock prism test, and the rock cylinder test C586 to selected Canadian aggregates are discussed. The chemical test C289 is shown to be unsatisfactory. The concrete prism test proved to be the most satisfactory, but it took up to two years to obtain results and its use is therefore impractical in many instances. A new accelerated test is proposed--The Rock Prism Test--a modified form of ASTM C586. Thin prisms of rock are vacuum saturated in alkali and the length change with time is recorded; results are obtained in about three months. Tests on similar rocks by the rock cylinder method C586 took up to two years. The new test would be useful for preliminary screening of potential aggregates to determine which would need further testing by the mortar bar or concrete prism methods.

Introduction

Canadian aggregates generally perform quite satisfactorily but there have been a number of reports of alkali-reactivity from various parts of the country. (The broad physiographic regions of Canada are shown in FIG. 1.) In the Western Cordilleran Region and on the Prairies cases of alkali-silica reactivity due to the presence of cherts and opaline silica in gravels are on record. Some impure dolomitic limestones from the St. Lawrence lowlands are alkali-carbonate reactive (Dolar-Mantuani (1,2), Swenson and Gillott (3), Gillott and Swenson (4)). In the Appalachian and Shield areas, precambrian granites, volcanics, schists, greywackes and quartzites are the most common rock types. Studies of the alkali reactivity of these rocks have been carried out by Dolar-Mantuani (5), Duncan et al (6), and Gillott et al (7). This paper deals with the alkali-silicate reactivity of rocks from the Canadian Shield and the

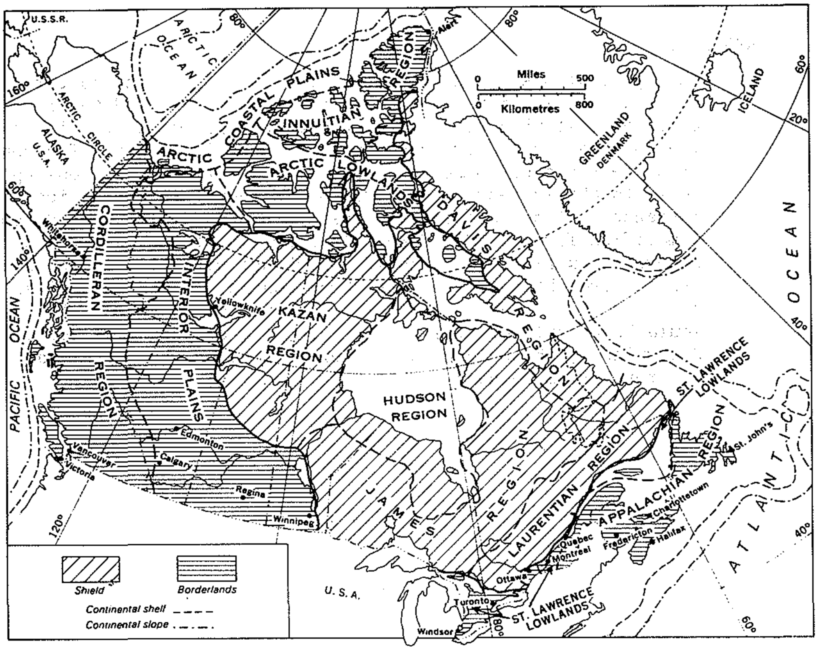

FIG. 1

Map of Canada showing the physiographic regions (from Geology and Economic Minerals of Canada, GSC, 1970)

Appalachian regions.

Glacial and fluvo-glacial gravels and sands are found overlying the bedrock in many regions but the deposits are usually quite localized. These gravels are a major source of aggregate but a variety of crushed rocks are also used.

Raw material for cement is found in most regions of Canada and cement plants are located adjacent to large urban centres. The composition of the cement varies but, with the exception of the West Coast region where low alkali cement is manufactured, normal Type I cement is a high alkali type with a total alkali content, expressed as Na_2O equivalent of between 0.6 and about 1%*.

Alkali-Silicate Reaction

In North America the term "alkali-silicate reaction" has come to be used to differentiate between the classical alkali-silica reaction as exhibited by opaline rocks and the reaction that occurs with quartzites, greywackes and phyllites that do not contain opaline or chalcedonic silica (see Gillott (8)). The expansion mechanism of alkali-silicate reactive rocks is not fully understood and although there is some evidence to the contrary, it is not at present clear that the mechanism is different from that of the classical alkali-silica reaction. The rate of the alkali-silicate reaction is slower than that of alkali-silica and the shapes of the expansion curves of rock cylinders of the two types in alkali may differ (FIG. 2). These differences may be due, however, to variations in the amount of reactive material present in the two rocks. The weight loss of the (alkali-silica) agate after 400 days was 35%; that of the alkali-silica reactive quartzite was less than 1% (9). It has also been suggested (7) that the expansion of some alkali-silicate rocks, e.g., argillite, may be due to the exfoliation of certain phyllosilicates but it is not clear at present if this is the only cause of expansion.

Test Methods

The following ASTM test methods have been and are used in the laboratory of the Division of Building Research, NRC, and by most Canadian workers:

C289	Quick Chemical Test	Modified C227	Concrete Prism Test
C227	Mortar Bar Test	Modified C586	Rock Cylinder Test

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*American Society for Testing and Materials, Standard Specification for Portland Cement Designation C150 (1970).

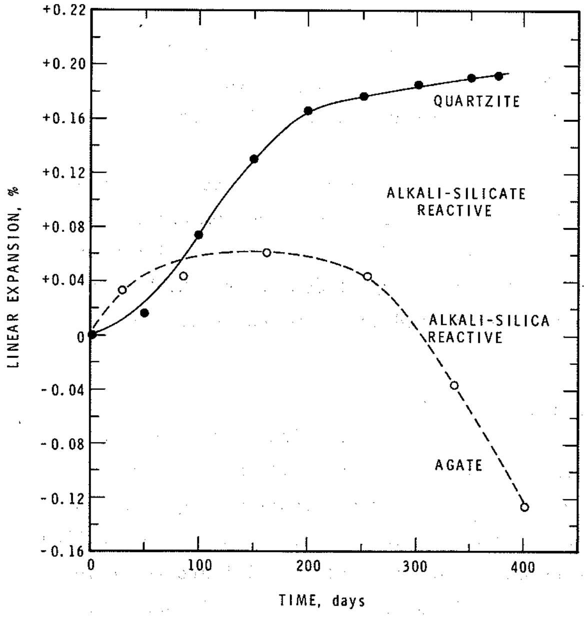

FIG. 2

Comparison between the expansion and contraction of alkali-silica and alkali-silicate rock prisms immersed in 2N NaOH at 20°C. Agate curve plotted from data from Duncan (9).

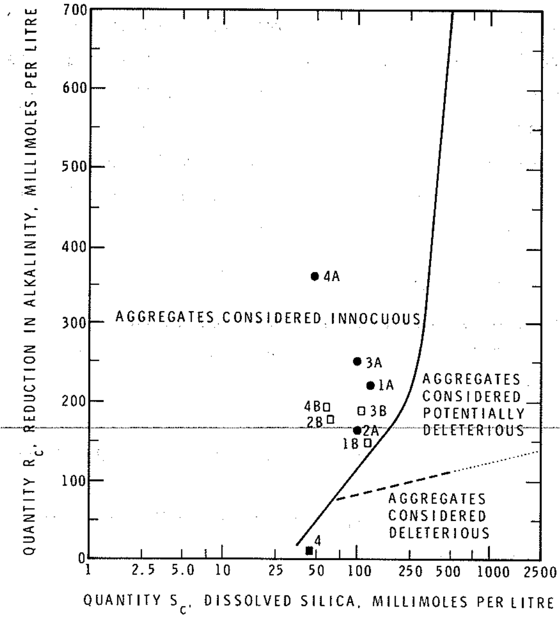

FIG. 3

Plot of results of quick chemical test C289 for a reactive sand of volcanic origin, Samples 1A, 2A and 3A and 4A and for a quartzite, Sample 5. 1B, 2B 3B and 4B are results of duplicate runs.

C289 Quick Chemical Test

This test was developed to assess aggregates believed to be susceptible to the classical alkali-silica reaction, although it has been demonstrated that it also works with some alkali-silicate rocks, e.g., a quartzite sample 5 (FIG. 3). Duncan et al (6), found only a 50% confidence factor for tests done on 14 rocks from Nova Scotia and concluded, therefore, that test C289 was inappropriate for rocks from the Appalachian Region.

If the mechanism of the alkali-silicate reaction is different from the classical reaction of alkali-silica, it is to be expected that the amounts of dissolved silica and reduced alkalinity observed in C289 should also be different. For example, a river gravel of volcanic origin which is known to be reactive was submitted to the C289 test. The results of runs on three pairs of samples are shown in FIG. 3, Nos. 1, 2 and 3, all of which

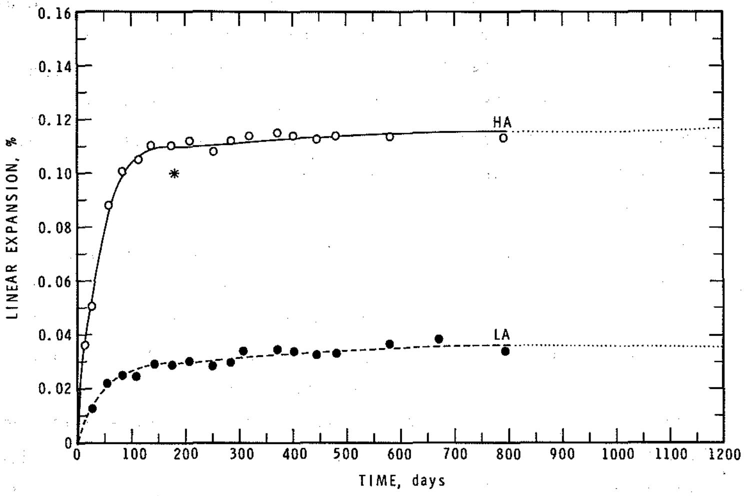

FIG. 4

Expansion of mortar bars, made from a reactive gravel of volcanic origin, with high and low alkali cement (H.A. & L.A.).

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*Indicates borderline between reactive and non-reactive aggregates as specified in ASTM Test C227.

plot in the non-reactive part of the diagram. The results of the mortar bar test (C227) on this gravel, shown in FIG. 4, clearly demonstrate that the gravel is expansive. The sand fraction of the material consists mainly of volcanic glass; the gravel-size fraction is composed of fragments of acid to intermediate volcanic rocks.

From tests carried out in the DBR laboratory and elsewhere, Duncan et al (6), it is evident that considerable caution is necessary in interpreting the results of the quick chemical test C289 when it is applied to potentially alkali-silicate reactive rocks.

Mortar Bar Test C227 and Concrete Prism Test

To overcome the objection to the mortar bar test, i.e., that mortar and not concrete is being tested, the concrete prism test was devised. It has been used extensively in Canada (6, 10) and in the DBR laboratory. The effective dimensions of the concrete prisms are 7.6 × 7.6 × 25.4 cm (3 × 3 × 10 in.). At DBR concrete prisms and mortar bars are routinely stored at 38°C and 100% relative humidity to accelerate the expansion. We have found the concrete prism test is the most satisfactory method of testing aggregates for alkali-reactivity but it has one major disadvantage which probably prevents its wider acceptance - the large amount of space needed to store the prisms. Only four prisms can be sealed in a container 28 cm in diameter by 47 cm high.

In the work at DBR there have been several instances when concrete prisms showed an aggregate to be expansive when the mortar test C227 did not; an example is shown in FIG. 5. The cement used is a normal Type I containing 0.34% Na_2O and 1.13% K_2O giving an Na_2O equivalent of 1.08%. The amount of soluble Na_2O and K_2O was determined by a modification of ASTM C114, about 30% of the sodium was soluble after ten minutes hydration; virtually all the potassium was soluble. This cement is classed as a high-alkali type according to ASTM Specification C150 but with an Na_2O content of 0.34% it is not very reactive. In future work, a cement with a higher Na_2O content will be used as it is known that Na_2O is more reactive than K_2O. A lower expansion for mortar bars than for concrete prisms has also been reported (10). (The work reported in this paper was also done in the DBR laboratories.) The reason for the discrepancy between the results of the mortar bar and concrete prism tests is still being investigated; the possibility that it may be due to the effect of grain size is being considered. Vivian (11) showed that the maximum expansion caused by

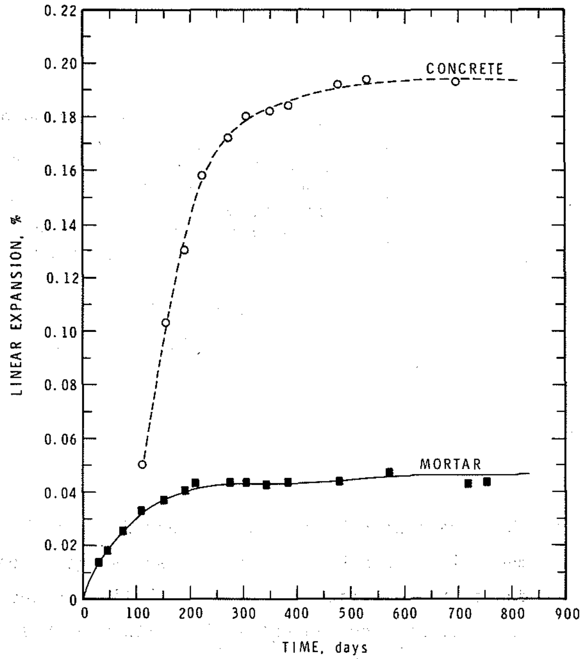

FIG. 5

Comparison of the amount of expansion of a mortar bar and a concrete prism made from a reactive feldspathic quartzite and high alkali cement.

additions of 5% opal to a non-expansive aggregate occurred where the grain size of the aggregate was in the range of 50 to 300 μm. It might also be expected that the maximum expansion of aggregate exhibiting alkali-silicate reactivity would also occur in the 50 to 300 μm range but Duncan (9) found that the amount of expansion increased as the average particle size was increased. For example, a calcareous argillite expanded 0.077% in 48 weeks when a normal grading (ASTM C227) was used but it expanded by 0.164% when the grading was altered by adding 65% of -9.5 + 4.76 mm material. This addition also increased the amount of the coarser material in the smaller screen sizes to give a total of 65% of coarser fractions compared to the standard grading.

In addition to the discrepancy noted between the expansion of mortar bars and concrete prisms, another problem was encountered. Mortar bars made from both high and low alkali cement showed the same (small) amount of expansion (FIG. 6). There is usually a significant difference in the amount of expansion observed in mortar bars made from reactive aggregate with high alkali and low alkali cement; for example FIG. 4 shows the expansions of mortar bars made from a reactive sand of volcanic origin.

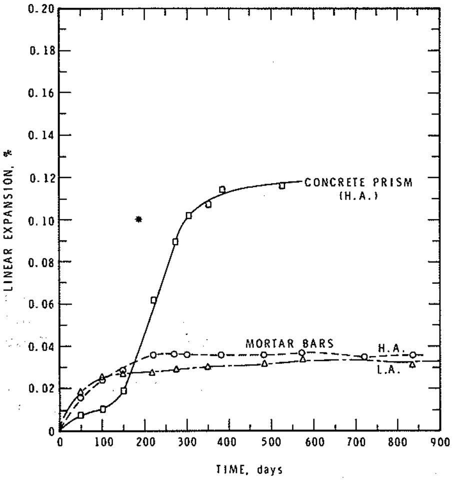

FIG. 6

Comparison of the expansion of mortar bars, of a reactive rhyolite, made with high and low alkali cement. For comparison, the expansion of a concrete prism made with high alkali cement is also shown.

H.A. High alkali cement

L.A. Low alkali cement

The reason why some mortar bars made with high alkali cement did not show more expansion than those made with low alkali cement has so far not been determined, but it may be due to the distribution of the alkalies in the cement - 0.34% Na_2O and 1.13% K_2O, Na_2O equivalent 1.08. Although this would be classed as a high alkali cement based on its Na_2O equivalent it may not behave as such in mortar. At DBR, for the past few years, washing the aggregate as specified in ASTM C227 has been omitted. In normal field practice the aggregate is not washed and it was thought that the test would better simulate normal usage if washing were omitted. The effect of omitting the washing of the aggregate is that about 0.8% more fine material is present, most of it in the 150 to 300 μ range. Experiments are currently in progress to determine if the small percentage of fines added to the mortar bars as a result of not washing the aggregates could act as a pozzolan and inhibit the expansion.

ASTM Test C227 specifies that expansion in excess of 0.1% at six months or 0.05% at three months be considered deleterious. This specification may be satisfactory for aggregates showing the classical alkali-silica reaction but is not reliable for concrete prisms made from aggregates that exhibit the alkali-silicate reaction. FIG. 7 shows the expansions of three concrete prisms made with high alkali cement and quartzites from the Canadian Shield. Samples 1 and 2 are excessively expansive; sample 3 is marginal. Quartzite 1 would be deemed excessively expansive by ASTM C227 specification but quartzite 2 would not, although it expanded more than 0.14% in two years and cracks had appeared in the prisms. Concrete prisms

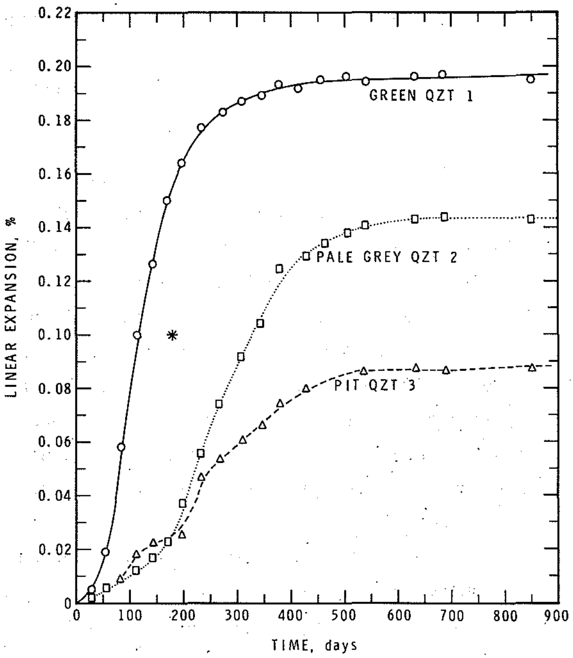

FIG. 7

Expansion curves of three concrete prisms made with quartzites and high alkali cement. Quartzites 1 and 2 are excessively expansive, number 3 is marginal. * Indicates borderline between reactive and non-reactive aggregates as specified by ASTM Test C227.

and mortar bars made with alkali-silicate reactive aggregates expand more slowly than those made from reactive alkali-silica rocks. Instead of setting a limit of 0.1% at six months as the boundary between reactive and non-reactive aggregates it would be better to specify the maximum expansion that should have occurred when the slope of the plot of percentage linear expansion vs time, as shown in FIG. 7, has flattened out. For the quartzites shown in FIG. 7, this occurred after about 600 days.

Modified Rock Cylinder Test, ASTM C586

Test C586 is to determine the potential expansivity of carbonate rocks, but Dolar-Mantuani (5) showed it to be applicable to a variety of Canadian alkali-silicate rocks. Duncan et al (6) found that the results of mortar bar and rock cylinder tests differed in only 11% of the samples studied, about the same disagreement as they found between the results of mortar bar and concrete prism tests. Recent results (6, 10) supported by DBR studies, show that the modified rock cylinder test is a satisfactory method to determine the potential expansivity of aggregates which may be expected to exhibit alkali-silicate reactivity. The modified rock cylinder test, when applied to potentially alkali-silicate rocks, has the same drawback as the mortar bar and concrete prism tests applied to these rocks, i.e., the length of time required to obtain results, frequently from one to two years. To be of practical value the rock cylinder test would have to be much more rapid.

Accelerated Test: The Rock Prism Test

Some time ago it was decided to try to develop an accelerated rock cylinder test. This was achieved by making small rock prisms 20 × 3.175 × 6.35 mm instead of the rock cylinders. The rock prisms were vacuum saturated with 2N NaOH solution at the start of the experiment. This new method, the Rock Prism test, will be described in more detail in a later publication. The length change of the rock prisms can be measured by one of two methods: (1) by a differential transformer giving a continuous chart readout; or (2) by means of a Huggenberger gauge which is read at selected intervals. (A rock prism and this gauge are shown in FIG. 8a. For comparison a regular rock cylinder is shown on a Tesa measuring apparatus in FIG. 8b.) Small metal studs are attached to the rock prisms to permit measurement with the Huggenberger gauge; these are visible in FIG. 8a. The studs are cemented to the rock with epoxy. Some problems

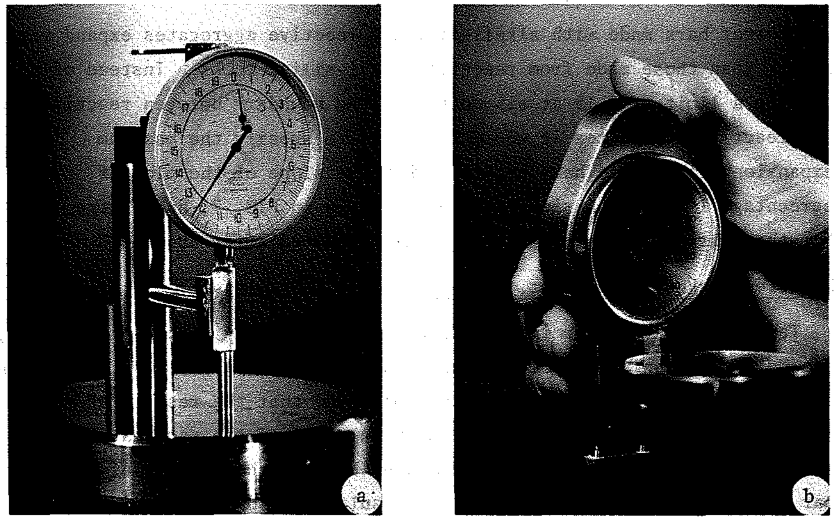

FIG. 8

a) Huggenberger gauge to measure length of rock prism. Note the two studs attached to the prism into which the prongs of the apparatus fit.

b) Tesa gauge to measure a rock cylinder.

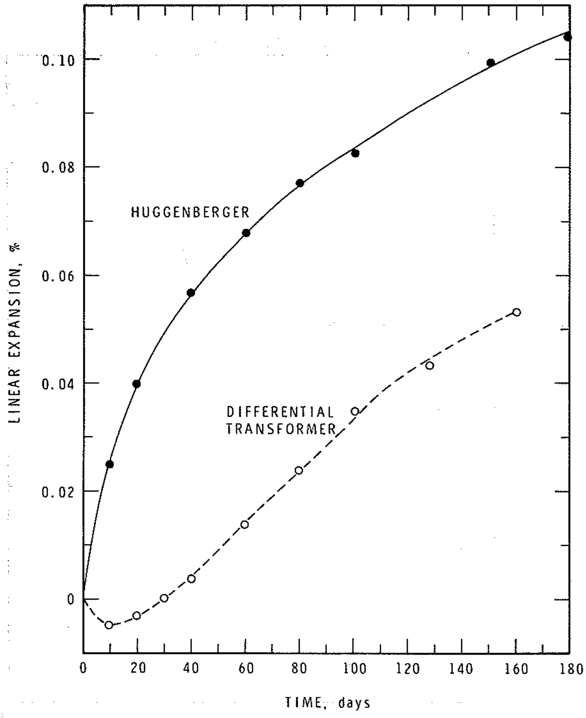

FIG. 9

Comparison of expansions measured on prisms of a reactive quartzite in 2N NaOH solution with a Huggenberger gauge and a differential transformer

were encountered due to the studs coming off, particularly on the more expansive samples but nonetheless satisfactory results were obtained. The differential transformer is capable of more accurate measurement, but it has the disadvantage that one apparatus is needed for each sample. In the transformer apparatus the sample is clamped in small jaws so there is no problem with epoxy becoming detached as sometimes happens to the studs on samples when the Huggenberger gauge is used. The results of expansion experiments with this gauge and transformer apparatus are shown in FIG. 9. Both curves show about the same slope but the amount of expansion after 100 days measured by the transformer is less than half that measured by the Huggenberger gauge. The discrepancy between the two samples may be due to differences in the two prisms or to friction in the transformer or

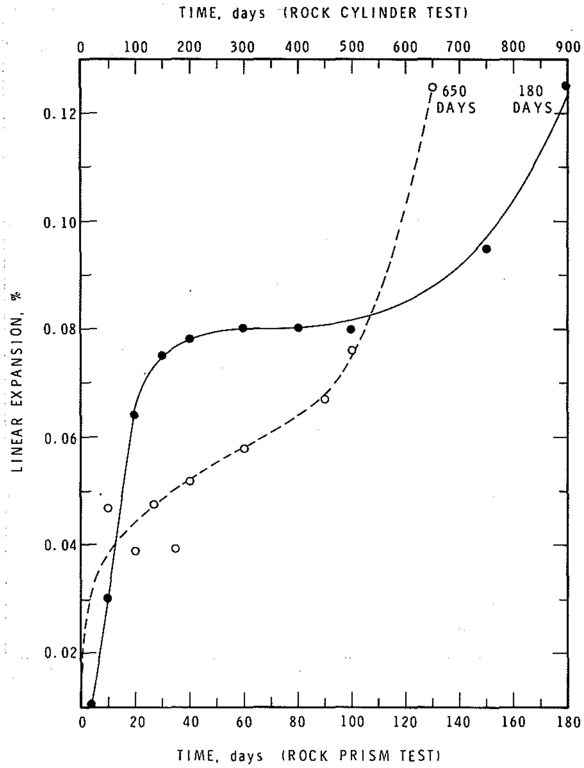

FIG. 10

Comparison of the rate of expansion observed on a rock prism and a rock cylinder of reactive quartzite immersed in 2N NaOH at 20°C.

both. The use of the differential transformer has been discontinued as the Huggenberger is more convenient.

The rate of expansion of a reactive quartzite measured with a Huggenberger gauge on a 20 × 3.175 × 6.35 mm rock prism and that measured on a rock cylinder 9 mm in diameter by 35 mm long with the Tesa gauge are shown in FIG. 10. The rock prism expanded by 0.08% in 60 days. This amount of expansion was not reached by the rock cylinder until after 500 days. There was almost a tenfold increase in the rate of expansion of rock prisms compared with rock cylinders.

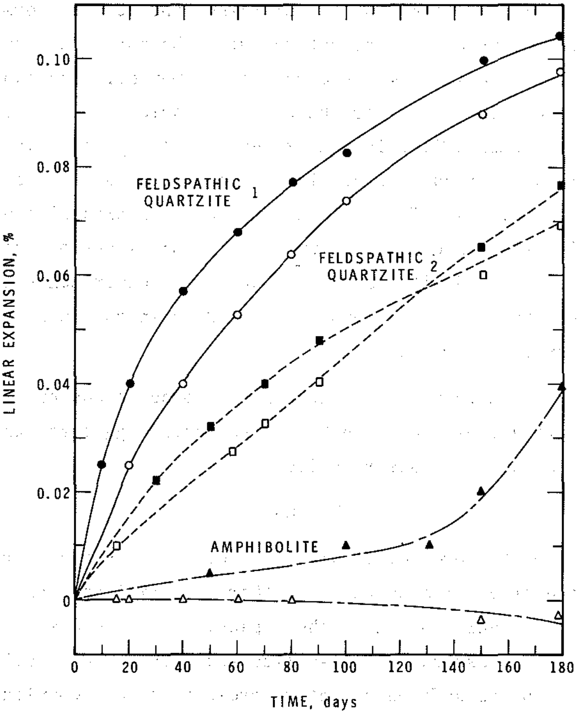

FIG. 11

Rock prism test on duplicate samples of aggregate immersed in 2N NaOH solution.

Pairs of cylinders, even though cored from the same piece of rock and immersed in alkali frequently show different rates of expansion due to lack of homogeneity in the sample. To try to reduce to a minimum this inhomogeneity in the pairs of rock prisms they were sawn side by side from the same slab of rock. Despite this, however, considerable variation in expansion was found between the pairs. Typical expansion curves for three pairs of rock prisms are shown in FIG. 11. The uncertainty that may arise in the interpretation of the rock prism test can be reduced by measuring three or more prisms from each sample. The effect of the lack of homogeneity of the rocks can be minimized by testing sets of prisms from a number of pieces of aggregate.

The problem of determining the dividing line between normal and expansive rocks, which was encountered with the mortar bar and concrete prism tests, also exists with the rock prism method. The two feldspathic quartzites shown in FIG. 11 are known from concrete prism tests to be expansive; the amphibolite is non-expansive. The problem is how to designate rocks that have curves lying between the quartzites and the amphibolite (FIG. 11). The dividing line between expansive and non-expansive rocks and the minimum duration of expansion experiments cannot be established with certainty until more experiments have been done on rock types that have previously been tested in concrete; work on this project is still in progress.

The rock prism test as outlined in this paper shows promise of providing a relatively rapid method of screening aggregate which may be potentially alkali-silicate reactive.

Discussion

Research on the problem of alkali-reactivity has been carried out for more than a quarter of a century but there is still no clear understanding of the exact mechanism by which the expansion of concrete occurs, even in the case of the classical alkali-silica reaction. The alkali silicate reaction, which was defined recently, presents a more complex problem. There is some evidence that expansion may occur due to several mechanisms. (For recent discussions on these topics see Diamond (12) and Gillott (8)). In studying the expansion of concrete made with reactive aggregate and high alkali cement there are two major questions to be answered: (1) How do rock prisms expand when immersed in alkali or in concrete, and (2) Why does the concrete itself expand and crack when made with reactive aggregate.

Gillott et al (7) demonstrated that some phyllosilicates expand when immersed in alkaline solution. The alkali dissolved out the interlayer precipitates thus increasing the surface area and allowing the adsorption of water which in turn caused the mineral to swell. This mechanism does not, however, explain the expansion of quartzites observed by the present authors. The quartzites consisted of large grains of quartz surrounded by interstitial fine quartz and silica.

The expansion of limestone and porous 96% silica glass was studied by Feldman and Sereda (13); the mechanism that they proposed to account for the expansion may well also apply to the quartzites. Essentially what happens is that the alkali reacts with silica or silicate to form an alkali-silicate hydrate which precipitates as a gel in the fine pores of the rock. This material has a high surface area and readily adsorbs water which causes it to expand (13). The characteristics of the adsorption and expansion isotherms confirm that the alkali-silicate hydrate is in the gel form.

The possibility of developing a reliable and rapid test for alkali-silicate reactive aggregates would be greatly enhanced if the mechanism or mechanisms of expansion were understood. Determining the cause of the expansion of concrete made with reactive aggregate and high alkali cement is complicated by three factors, in addition to the alkali-silicate reaction: temperature, moisture content, and hydration reaction. The aim of the test for alkali-expansivity is to determine the effect of the alkali-silicate reaction alone on the expansion of the concrete. This is never a simple task; it is often an impossible one. In the initial period just subsequent to fabrication all four parameters change simultaneously and feed-back problems arise. As hydration proceeds the temperature rises and the moisture content decreases due to changes of relative humidity. It is very important to keep these facts in mind both in the design and evaluation of test procedures.

Acknowledgements

The authors are indebted to P.J. Sereda for discussions concerning the reaction mechanism, and to J.P. Lefebvre and H. Schultz for the care with which they made and measured the samples.

This paper is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division.

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CONTRIBUTIONS TO DISCUSSION

Mr. B. Mather

I suggest that the term "alkali-silicate reaction" be reserved for reactions with phyllosilicates as will be suggested by S. Diamond (in press) rather than used for reactions that involve the classical alkali-silica physical chemistry - differing only in rate of development and shape of curve.

Dr. G.M. Idorn

In order to distinguish between the different types of reactivity we are concerned with one must consider the character of the reactive rock closely.

Tense and porous flints are 100 percent mono-mineralic silica rocks. Dense flint particles often have interior regions less compact than other parts and are thus attractive for alkali silica reaction to start in. Expansion therefore often perform as sudden crack formation within the rock particles and then continuing out through the surrounding paste. Porous flint particles often become completely transformed to gel, before expansive pressure from the remaining "gel-body" is exerted upon the surrounding paste and makes it crack (or makes the gel escape out as a diluted liquid into the pores of the paste without causing cracking).

Polymineralic rocks - phyllites, greywackes etc. behave differently. The reacting constituents are silica and maybe also silicates occurring as interstitial minerals, and the reaction with alkalies affect only their areas of the rock particles. Cracking therefore also originates in reactive areas of the particles.

Crushing of coarse aggregate specimens in order to make sand for standard mortar bars will make the dense flint sand consist of more and less readily reactive particles, porous flint to remain unchanged with regard to reactivity, and polymineralic rocks to consist of reactive and innocuous sand particles, respectively. Accordingly the mortar bar test experiments must be interpretated with great care, if intended to reveal information on the nature, characteristics and designation of alkali-reactivity.

Dr. G.M. Idorn (cont.)

I do not think this is in opposition to P. Gratton-Bellew's designation. Alkali-silica and alkali-silicate reaction, but that thoroughness and consistency is called for when such designation is to be established.

Mrs. K. Mather

The point made by Dr. Idorn is excellent because he reminds us that we should pay attention to the minute geography of the aggregate particles. I am also reminded by Dr. Gratton-Bellow's comment of the aggregate in Fontana Dam; the aggregate graded from coarse-grained greywacke to fine-grained phyllite without much change in composition. We counted the number of coarse aggregate particles associated with gel pockets, reaction rims, and internal cracking, and we sorted these by lithologic variety. We found that there was more gel and more internal cracking associated with the coarse-grained rocks rather than with the fine-grained rocks. This is not the condition that exists with rocks from the Canadian shield.

Dr. P. Gratton-Bellew

In reply to questions and comments on our paper.

Mrs. K. Mather and Dr. Idorn raised the problem of the effect of grain size of rock aggregate on the expansion of mortar bars and concrete prisms, and of pore size and distribution and surface area. unaffected by grain size in the range considered (3mm - 0.1mm). However in reactive quartzites large grains are surrounded by finer siliceous material and fine quartz, possibly in the coarser material more of the fine interstitial material (thought to be the reactive component) may occur on the surface of quartz grains and so enhance the reactivity of the rock.

In discussion with B. Mather and G. Idorn on use of the term alkali-silicate reaction. This term I used loosely to refer to a variety of rock types - this usage is probably misleading and I agree with B. Mather that the term alkali-silicate reaction should be reserved for the explanation of phyllosilicates. reported by Gillot if this is indeed the cause of expansion of the aggregate in these cases. The term alkali-silicate should also surely be applied and reactions such

<u>Dr. P. Gratton-Bellew</u> (cont.)

as the one I described as the paper concerning the expansion of concrete made with a sand of volcanic origin and consisting largely of volcanic glass - a silicate material.

ADDENDUM - THE EFFECT OF CEMENT MIXTURES ON ALKALI EXPANSION

Dr. G. Gudmundsson and H. Ásgeirsson

Further to the data presented at the Reykjavík Symposium[1)] we are now able to make a minor addendum.

Firstly, it may be mentioned, that we have continued measuring our mortar bars, and found that little change has taken place in the volume of our pozzolanic mortar prisms. All the tested samples proved to be of effective pozzolans as far as reduction in mortar bar expansion is concerned; yet there is a decisive difference in the strength increase (see Fig. 1).

It is clear that the scale used for expansion in Fig. 1 greatly exceeds the exactness of measurements; it may though in all fairness be stated that a 25% pozzolan replacement of the cement in the reference sample reduces its 12 months expansion from approximately 0,2 to about 0,02% (0,179 to 0,021 ave.).

Contrary to what is often stated we find no correlation between the acidity of the pozzolans and their activity. Moreover, some of the most basic samples have proved to posess the strongest pozzolanic properties (No 14). Sæmundsson[2)] has classified the rocks into basaltic, andesitic/dasitic and rhyolitic composition, as shown in Fig. 1; but neither this nor other sequence arrangements have revealed direct conformity. All slections of materials must therefore be subject to imperial test results.

If, however, the results illustrated in Fig. 1 are compared with those obtained from the ISO/863-1968 (E) - Recomended tests, a fairly good agreement is observed[1)] (Fig. 2). The samples appearing on or near the border parameter (3, 11, 5) in the ISO-diagram also show the lowest increase in strength;

and those that fall lowest on the diagram are also the strongest pozzolans according to the mortar bar tests.

We mentioned the gravity of our domestic situation last year; since we were producing cement of very high alkalinity and using reactive glassy aggregates. However, we had not suffered extensive damage, and pointed out that the wet and cool climate might be our safeguard. Sidney Diamond and Harold Vivian[3] pointed out to us that the viscosity of the gel formed in our concrete might be lessened by the very high alkalinity, and this could then explain the minimal damage. A partial use of low-alkali-cement might therefore bring about a pessimum alkali content and disruptive damage. We therefore carried out the examination we illustrate in our 3rd Fig. Expansion appeared in this examination to be in direct proportion with alkali content. Such studies however need to be carried further.

Even though alkali-aggregate damage cannot be said to be common it certainly exists locally. This may be seen on Fig 4 to 7, which show damage to exterior walls to a bungalow in the Reykjavík area. Even though these damages originate primarily from exceedingly reactive aggregate particles, they certainly serve to remind us of the grave situation we face.

References:

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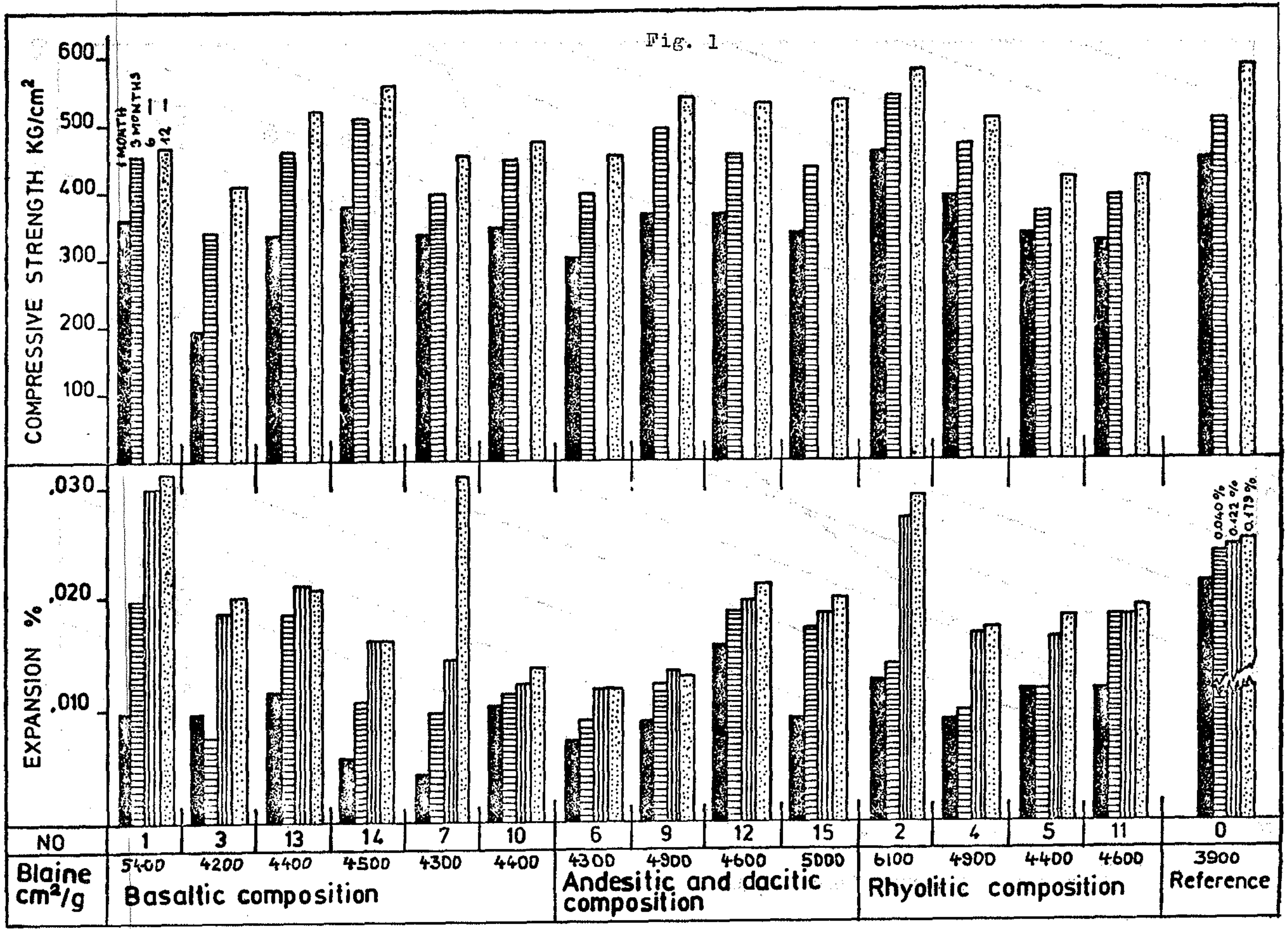
3) H. Ásgeirsson, An Epilogue, ibid, p. 269-270.

Fig. 1


COMPRESSIVE STRENGTH KG/cm²
600
500
400
300
200
100
1 MONTH
3 MONTHS
6 —
12 —
EXPANSION %
,030
,020
,010
0.040 %
0.421 %
0.179 %
NO
1
3
13
14
7
10
6
9
12
15
2
4
5
11
0
Blaine cm²/g
5400
4200
4400
4500
4300
4400
4300
4900
4600
5000
6100
4900
4400
4600
3900
Basaltic composition
Andesitic and dacitic composition
Rhyolitic composition
Reference

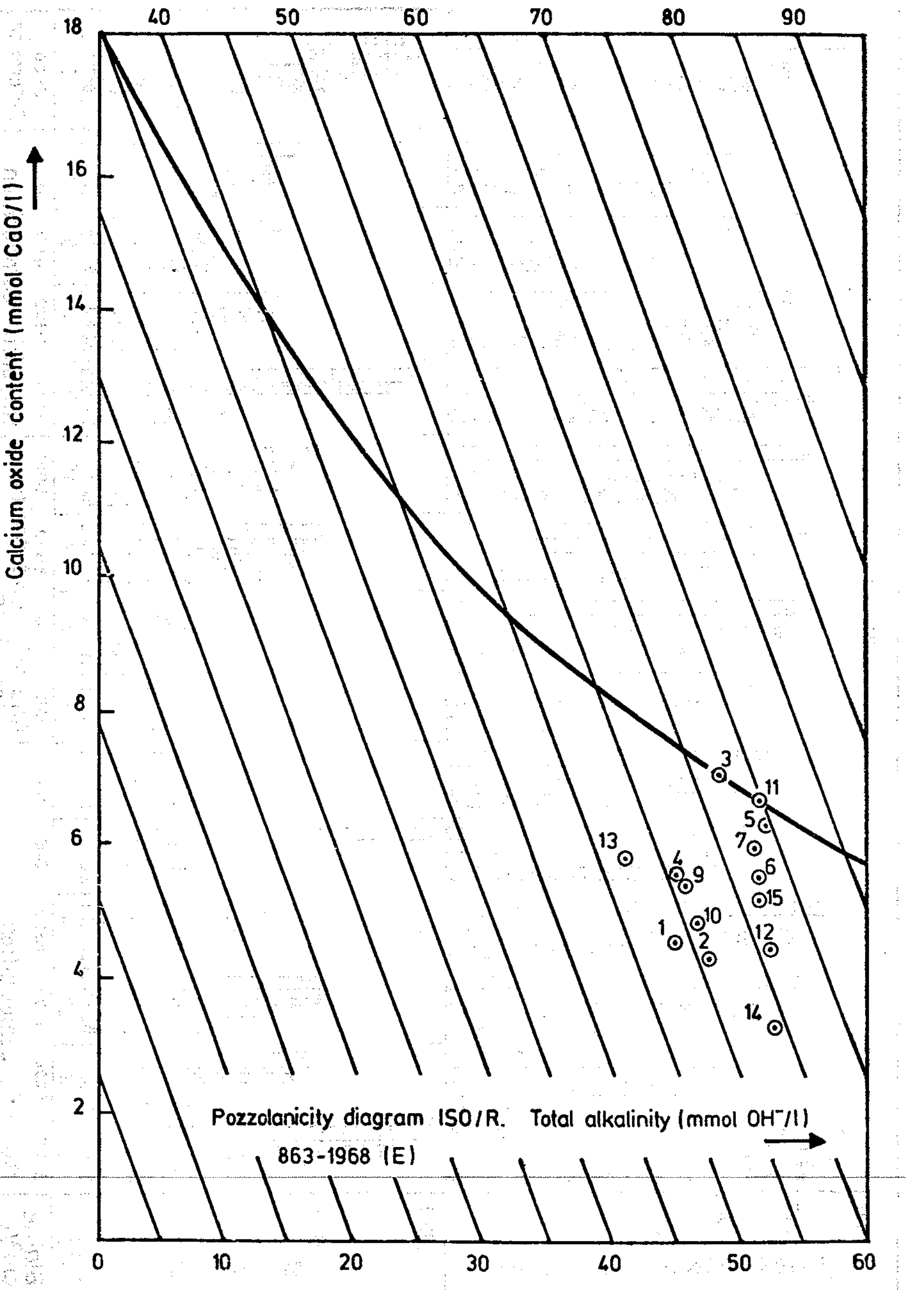

Calcium oxide content (mmol CaO/l)
18
16
14
12
10
8
6
4
2
40
50
60
70
80
90
0
10
20
30
40
50
60
Pozzolanicity diagram ISO/R. 863-1968 (E)
Total alkalinity (mmol OH⁻/l)
1
2
3
4
5
6
7
9
10
11
12
13
14
15

Fig. 2

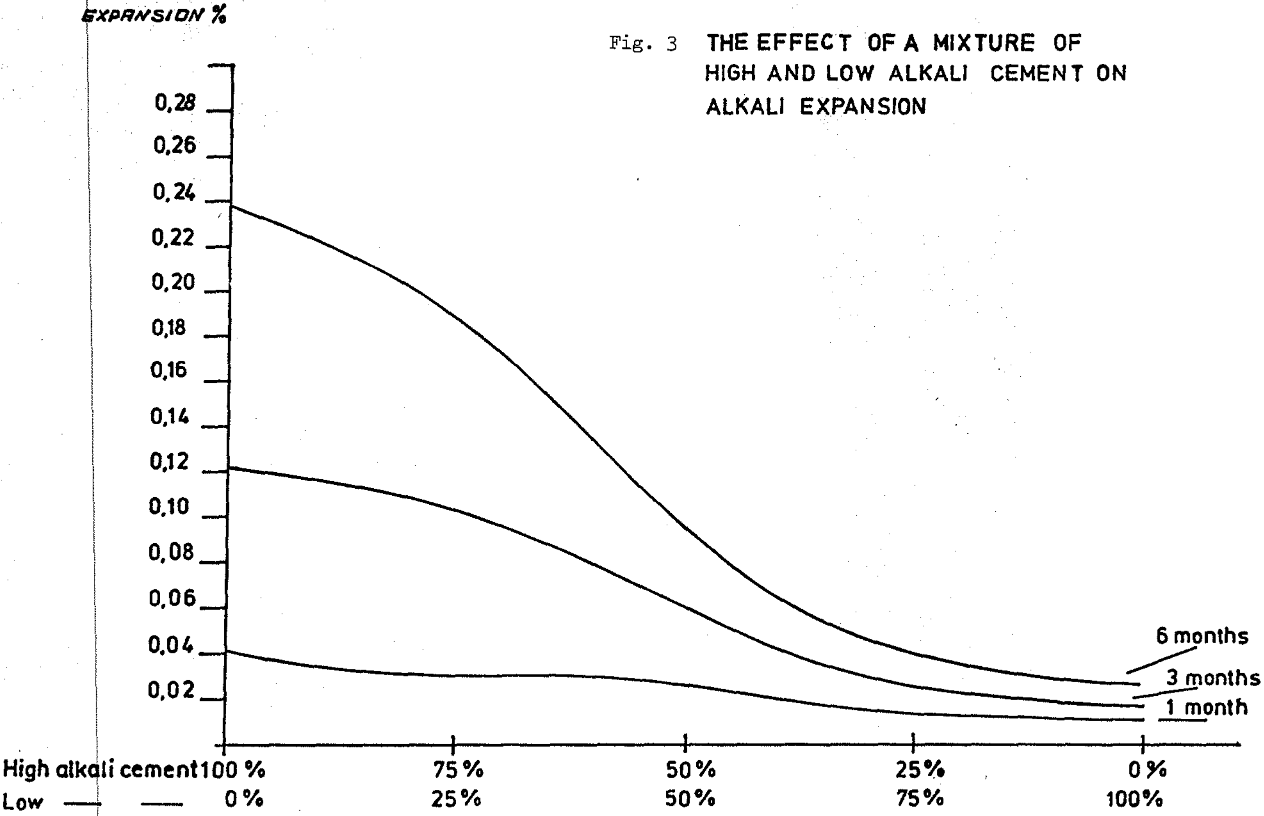


Fig. 3 THE EFFECT OF A MIXTURE OF HIGH AND LOW ALKALI CEMENT ON ALKALI EXPANSION

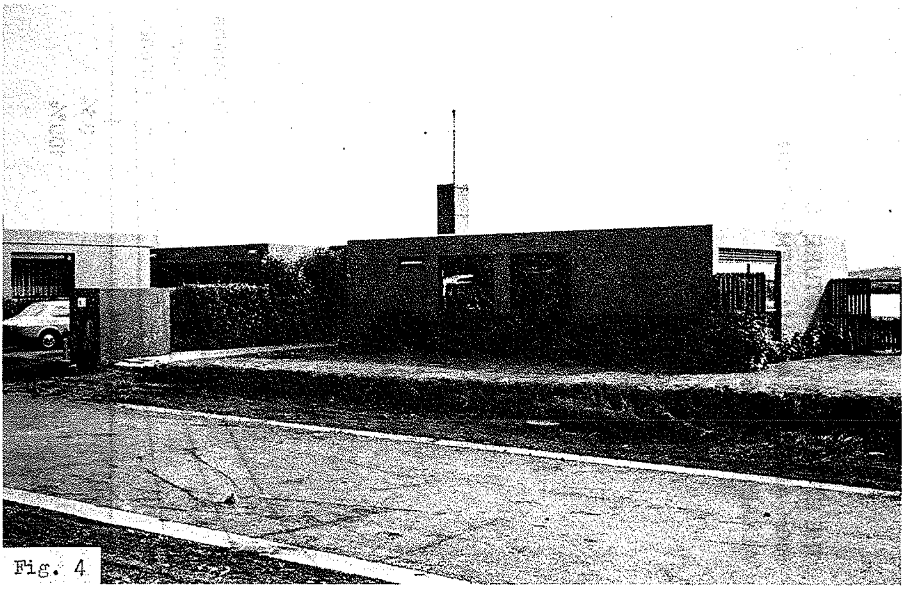


Fig. 4

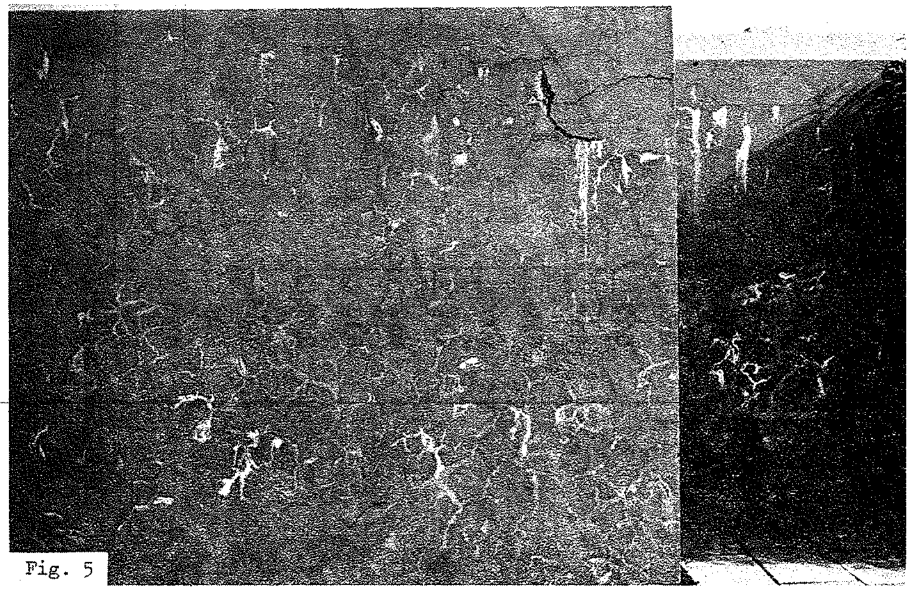


Fig. 5

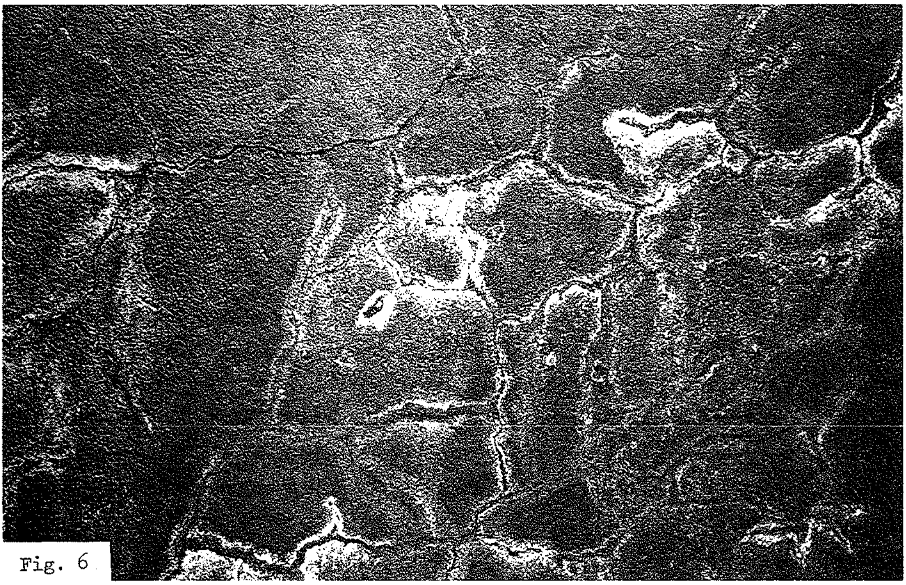


Fig. 6

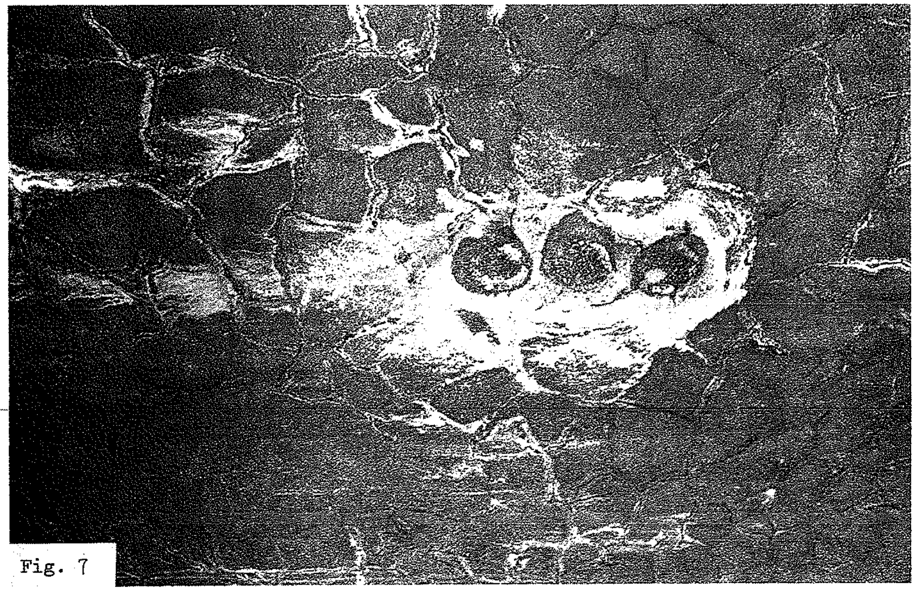


Fig. 7

CONTRIBUTIONS TO DISCUSSION

Mr. D. St.John

Did you check your pozzolans used for tests by water demand tests, or carry out any particle size distribution measurements. It has been our experience that surface area does not adequately characterise a fine material.

Dr. H. Asgeirsson

In reply to the various enquiries arising from discussion I would like to record that the high alkali cement contained 1.5% sodium equivalent and the low alkali cement about 0.35%. The cement content was approximately 350 Kg/m^3 and that Smidt Hammer and core tests proved that the strength of the concrete is still quite high in spite of the cracks. No data is available on the tests suggested by Mr. D. St.John.

The Ladies Party at C. & C. A.

ON THE ALKALI-CARBONATE REACTIVITY OF AGGREGATES FROM IRAQI QUARRIES

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Department of Geology

ABSTRACT

The potential reactivity of carbonate rocks for concrete aggregates is investigated in samples collected from twenty eight quarries, distributed over different parts of Iraq, according to the ASTM: D 75-71. The samples were examined petrographically according to the ASTM: C 295-65, and analyzed chemically for major constituents ($CaCO_3$, $MgCO_3$, and insoluble residue). The samples were also subjected to mortar bar test according to the ASTM: C 227-71; the rock-cylinder test according to the ASTM: C 586-69; and the compressive strength according to the ACI Code 318-56. The concrete mixes were prepared from a low alkali cement (Sarchinar factory) and a high alkali cement (Kufa factory) and the results were compared. The results of the four tests carried, were utilized to give a combined evaluation to the carbonate aggregates from the quarry sites studied. This evaluation will be a useful guide in the choice of suitable crushed carbonate aggregates in situations where gravel and sand deposits are not available or of low quality.

The Alkali-Carbonate Reaction

Two types of alkali-aggregate reactions in concrete are now well established, namely: the alkali-silica reaction and alkali-carbonate rock reaction. A survey of alkali-silica reaction in Iraqi quarries was carried by the senior author(1).

The effect of alkali-carbonate rock aggregate reaction in concrete deterioration was first established in (1957) in the vicinity of Kingstone, Ontario, where an argillaceous dolomitic limestone was involved in the reaction (2).

A differentiation should be made between expansive alkali-carbonate rocks reaction and those reactions developing reaction rims around certain carbonate rock aggregates. The expansive aggregates cause deterioration of concrete by cracking and consequent failure. The rim developing carbonate aggregates cause deterioration by its weathering effect and decline in physical quality of the aggregate and consequently of the concrete (3,4).

The most pronounced reaction known to occur in carbonate aggregates is called as "Dedolomitization". It is a reaction in which the dolomites of the carbonate rocks are attacked by the alkalis of the cement, and accompanied by the development of calcite, and appearance of brucite (5).

The rim-developing carbonate rocks are generally of the same mineral composition and texture as the expansive rock but relatively of lower insoluble residue content and higher dolomite content (6).. The rim zones, were found to be less porous and contain more silica than the interior of the carbonate aggregate particles (3).

A general study of alkali-aggregate reaction in the Middle East was carried during the last two years (7,8,9).

The factors influencing the alkali-carbonate reaction include the cement alkali content (2), the expansive reactivity of rocks (6) the temperature and moisture condition (6), the maximum aggregate size (2), and the porosity and permeability of aggregates (10).

Different methods and approaches were suggested to overcome the reactivity by various workers among which were (11,12, 13, 14).

Methods of Test

A. Petrographic test:

Petrographic examination contributes in several ways to the investigation, selection, testing, and control of aggregates. Preliminary examination of concrete aggregates is performed either in the field or in the laboratory as an adjucent to examination, exploration, and sampling. This may help in locating relative quality and potentially reactive rocks in the field (15).

A recommended practice for petrographic examination of aggregate for concrete is given by ASTM Designation C295.

B. Mortar bar test:

A standard method of test for potential alkali reactivity of cement-aggregate combinations is described in ASTM Designation C 227. The method covers the determination of the susceptibility of cement-aggregate combinations to expansive reactions involving the alkalies (Na & K) by measurement of the increase (or decrease) in length of mortar bars containing the combination during storage under prescribed conditions of test.

C. Rock-cylinder test:

In this type of test either a small rock-cylinder or rock-prism is immersed in 1 to 2 m solutions of alkali. The time needed for this test to yield significant results is from two to six weeks, depending on size of the specimen, concentration of alkali, and reactivity of aggregate (16).

D. Compressive strength test:

The rim-developing rocks in concrete has a determinative effect on strength development. A decline in strength may results when a large proportions of such carbonate rocks are present (3, 6).

Geology of Carbonate Rocks in Iraq

The limestones and dolomites are distributed throughout large parts of Iraq ranging in age from the Devonian to the Miocene. They occur in various forms such as: pure limestones;

marly limestones; dolomitic limestones and pure dolomites. Their geologic formations greatly vary in thickness, extent, or shape, depending on the type of depositional basin, its extent and configuration. Other factors includes rate of deposition, time, and source area. The formations of northern Iraq are generally thicker than elsewhere, this is because of the relatively deeper basin of deposition.

The quarries sampled as shown in figure (1) are of different types depending on the position of the stratigraphic section with respect to the ground surface. This is greatly controlled by the tectonic history of the area.

Quarries of northern Iraq are almost of open shelf type because the area is affected by intensive tectonic movements. Some parts of the western desert are also of open shelf type, while the quarries of river plain are generally of open pit type. Table 1 gives a brief description of the quarry sites investigated.

Despite the original type of rock (chemical, biochemical, or detrital), the limestone and dolomite may be often surface altered to a hardpan by a diagenetic process, which may leads to the concentration of salts near the surface; this frequently occurs in the Middle East countries where evaporation exceeds precipitation (8).

Finally, a complexity in the geology of an area may leads to the complexity of alkali-reaction study, because the rock greatly vary in composition and different kinds of reaction occur (17).

Data Interpretation

Results of petrographic test:

From all studied samples, only two samples showed evidences of deleterious alkali reaction. These includes: Haditha (a) and Rutba (c) calcitic dolomites. These two samples were confirmed to be generally of the same petrographic characteristics. Haditha (a) aggregate have relatively higher insoluble residue but lower dolomitic content.

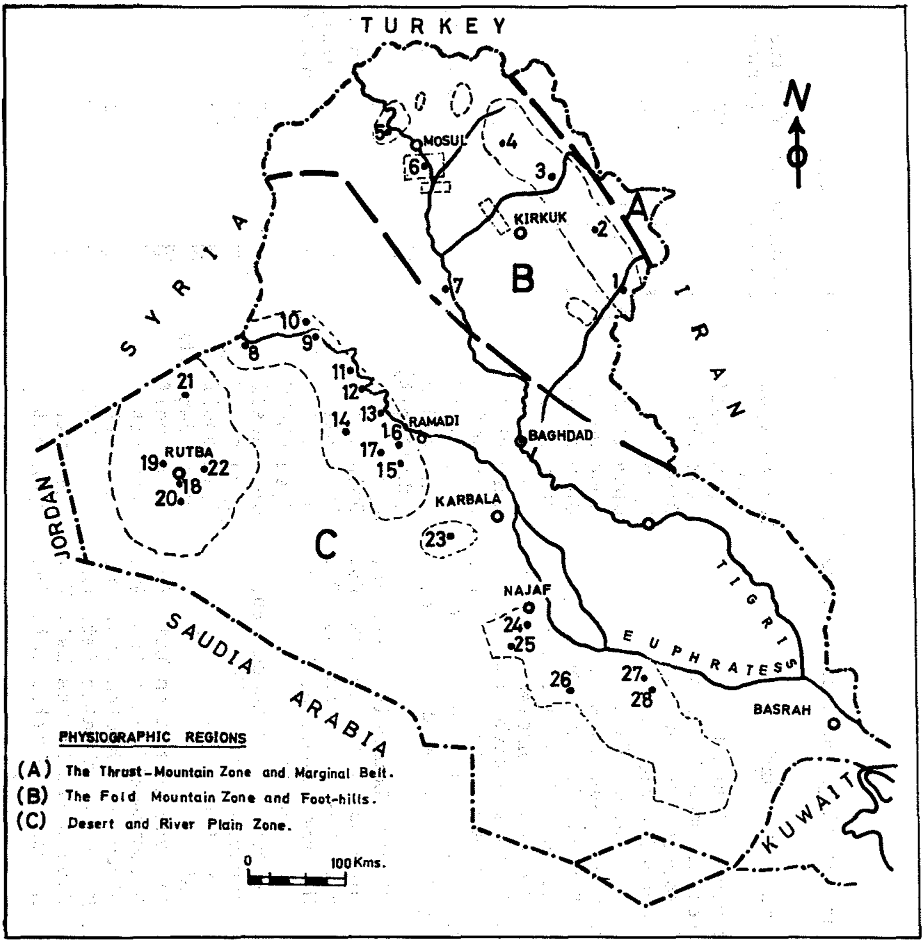

Fig.(1). Physiographic map of Iraq showing areas of major quarriable carbonat rocks and locations of the investigated quarry sites.

Table (1): Brief outline of the investigated quarry sites (see figure 1 for locations).

No.	Quarry name	Geologic Formation	Quarry type	Physiographic region	thickness (meters)
1	Derbendikhan	Eocene-Pilaspi Fn.	Open shelf	Fold Mountain and Foothills zone	70
2	Sarchinar	Cretaceous-Shiranish Fn.	Open shelf		20
3	Dokan	Cretaceous-Shiranish Fn.	Open shelf		70
4	Salah Al-Din	Eocene-Pilaspi Fn.	Open shelf		30
5	Badosh	M. Miocene-L. Fars Fn.	Open shelf		3
6	Hammam Al-Alil	M. Miocene-L. Fars Fn.	Open shelf		4
7	Baiji	M. Miocene-L. Fars Fn.	Open shelf		5
8	Ghussaiba (a,b)	L. Miocene-Euphrates Lst. Fn.	Open shelf		6
9	Rawa (a,b)	L. Miocene-Euphrates Lst. Fn.	Open shelf		5
10	Anah (a,b)	U. Oligocene-Anah Lst. Fn.	Open shelf		10
11	Haditha (a,b,c)	L. Miocene-Euphrates Lst. Fn.	Open pit	Desert and River Plain Province	3
12	Khan Baghdadi (a,b,c,d)	Euphrates and Anah Lst. Fn.	Open shelf		vauable
13	Hit (a,b,c,d,e)	Euphrates and Anah Lst. Fn.	Combined open (shelf+pit)		vauable
14	Kubbaisa (a,b)	L. Miocene-Euphrates Lst. Fn.	Open shelf		8
15	Abu-Sfayya (a,b)	L. Miocene-Euphrates Lst, Fn,	Opin pit		vauable
16	Kilo 45	L. Miocene-Euphrates Lst. Fn.	Open pit		vauable
17	Kilo 60 (a,b)	L. Miocene-Euphrates Lst. Fn.	Open pit		vauable
18	Wadi Msad	Cretaceous-Msad Fn.	Open shelf		1.5
19	Rutba (a,b,c)	Cretaceous-Um Er Rhduma Fn.	Open shelf		20
20	Tayarat	Cretaceous-Tayarat Fn.	Open shelf		20
21	Wadi Swab	Eocene-Dammam Fn.	Open shelf		15
22	Wadi Horan (a,b,c,d,e)	Recent	river deposits		-
23	Shithatha (a,b,c,d)	L. Miocene-Euphrates Lst. Fn.	Open shelf		8
24	Qalat Mazlum (a,b)	L. Miocene-Euphrates Lst. Fn.	Open pit		1
25	Haiydia (Najaf)(a,b)	L. Miocene-Euphrates Lst. Fn.	Open pit		1
26	Shanafia (a,b,c)	L. Miocene-Euphrates Lst. Fn.	Open shelf		2
27	Samawa 1 (a,b)	L. Miocene-Euphrates Lst. Fn.	Open pit		1
28	Samawa 2 (a,b)	L. Miocene-Euphrates Lst. Fn.	Open pit		3

Results of Mortar Bar Test:

The percent linear expansion curves of mortar bars for the different quarry samples with high alkali Kufa factory cement, (1.06% Na_2O total) are shown in figures 2a,3a,4a,5a,6a,7a,8a, and 9a respectively.The percent linear expansion curves of mortar bars for the different quarry samples with low alkali Sarchinar factory cement(0.48% total Na_2O) are shown in figures 2b,3b,4b,5b,6b,7b,8b and 9b respectively. A direct comparasion can be made between the expansion curves for the different samples with high and low alkali cement.

The relatively more expanding mortar bars are those obtained from quarries west of the Euphrates river and the Western desert. Samples obtained from quarries from northern and southern Iraq were generally non or slightly expansive.

The effect of the dilution of the mortar mix of expansive Haditha aggregate with the inert Sarchinar aggregate yeilded some reduction in expansion ,but the deleterious effect remained. Figure 10 shows a comparasion between three haditha mortars prepared from low alkali cement,high alkali cement and a diluted sample with high alkali cement .

Results of Compressive strength test :

There was no observed decline in the rate of compressive strength development with time in all the concrete cubes prepared from all the aggregate types.The rate of compressive strength growth was noticed to be different in different samples. The following quarry site samples gave not accepted strength values in 28 days:Haditha,Haiydia,Ghussaiba,Qalat Mazlum,Samawa 2, Kilo 60,Rawa ,Baiji and Badosh.

Results of petrographic examination of the mortar concrete:

All of the mortars prepared from low and high alkali cement were examined petrographically, and not found to reveal any reaction criteria with the exception of three samples from Haditha,Rutba and Tayarat.Microcracks of appreciable lengh were noticed in Haditha and Tayarat mortar;while the Rutba mortar revealed clear reaction rims .

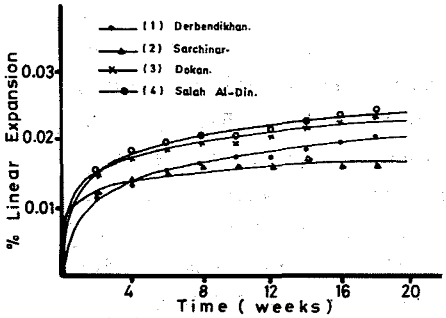

Fig.(2a). Percent linear expansion of mortar bars versus time using Kufa cement (quarry sites 1, 2, 3 & 4).

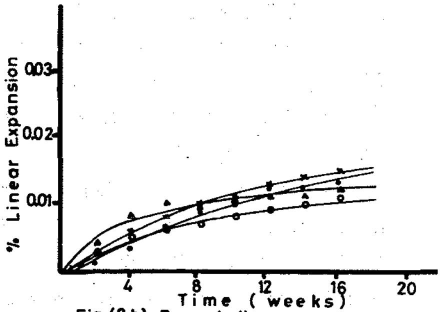

Fig.(2b). Percent linear expansion of mortar bars versus time using Sarchinar cement (quarry sites 1, 2, 3 & 4).

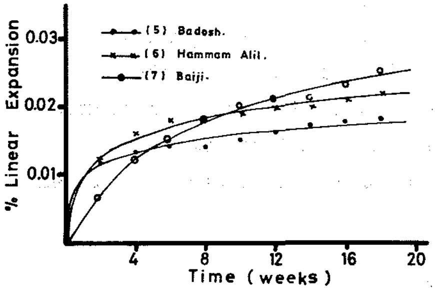

Fig.(3a). Percent linear expansion of mortar bars versus time using Kufa cement(quarry sites 5, 6 & 7).

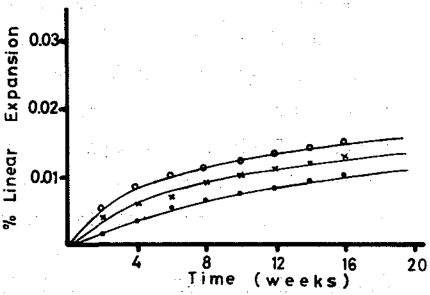

Fig.(3b). Percent linear expansion of mortar bars versus time using Sarchinar cement (quarry sites 5, 6 & 7).

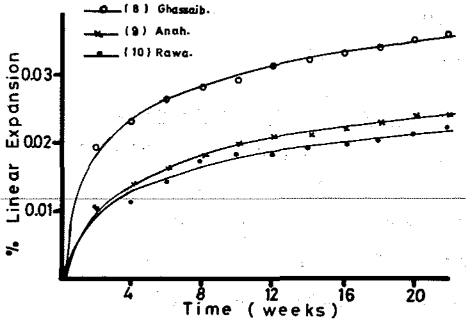

Fig.(4a). Percent linear expansion of mortar bars versus time using Kufa cement (quarry sites 8, 9 & 10).

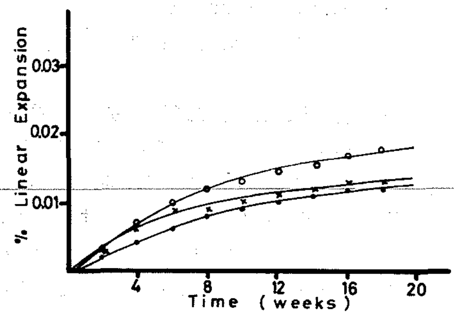

Fig.(4b). Percent linear expansion of mortar bars versus time using Sarchinar cement (quarry sites 8, 9 & 10).

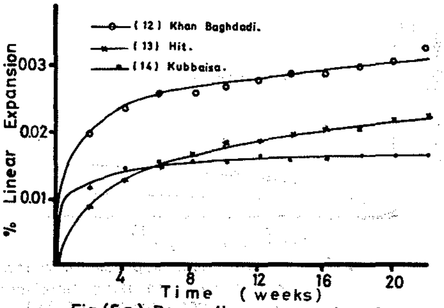

Fig.(5a). Percen linear expansion of mortar bars versus time using Kufa cement(quarry sites 12,13 & 14).

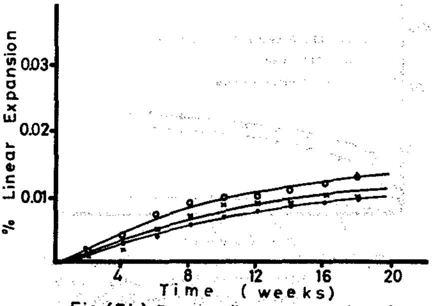

Fig.(5b). Percent linear expansion of mortar bars versus time using Sarchinar cement (quarry sites 12, 13 & 14).

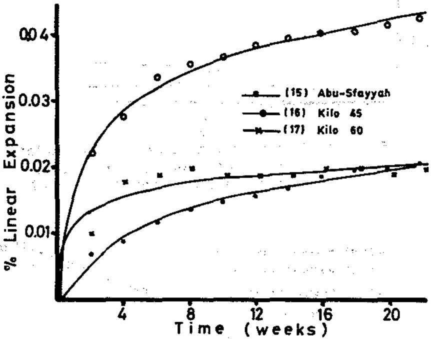

Fig.(6a). Percent linear expansion of mortar bars versus time using Kufa cement (quarry sites 15, 16 & 17).

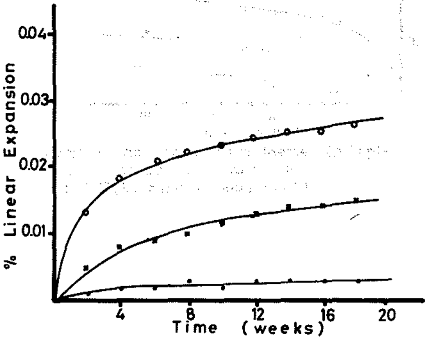

Fig.(6b). Percent linear expansion of mortar bars versus time using Sarchinar cement (quarry sites 15, 16 & 17).

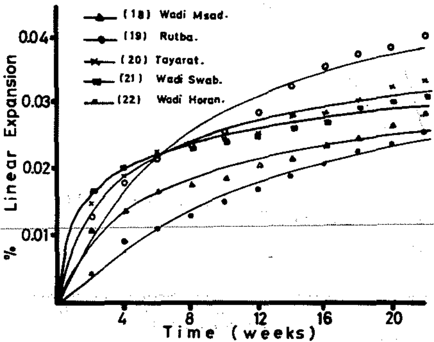

Fig.(7a). Percent linear expansion of mortar bars versus time using Kufa cement (quarry sites 18, 19, 20, 21 & 22)

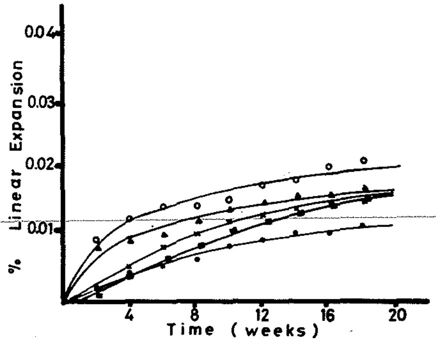

Fig.(7b). Percent linear expansion of mortar bars versus time using Sarchinar cement (quarry sites 18, 19, 20, 21 & 22).

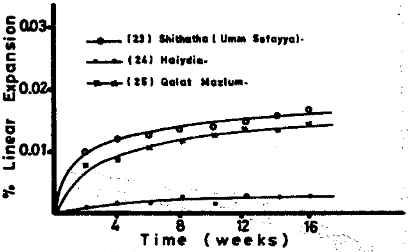

Fig.(8a). Percent linear expansion of mortar bars versus time using Kufa cement (quarry sites 23, 24 & 25)

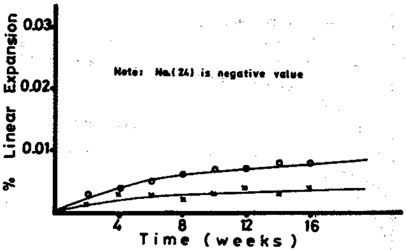

Fig.(8b). Percent linear expansion of mortar bars versus time using Sarchinar cement (quarry sites 23 & 25)

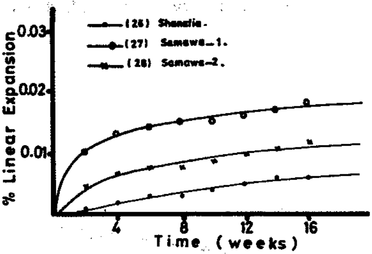

Fig (9a) Percent linear expansion of mortar bars versus time using Kufa cement (quarry sites 26, 27 & 28)

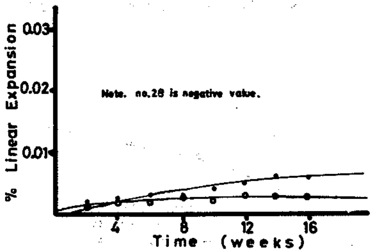

Fig (9b) Percent linear expansion of mortar bars versus time using Sarchinar cement (quarry sites 26 & 27)

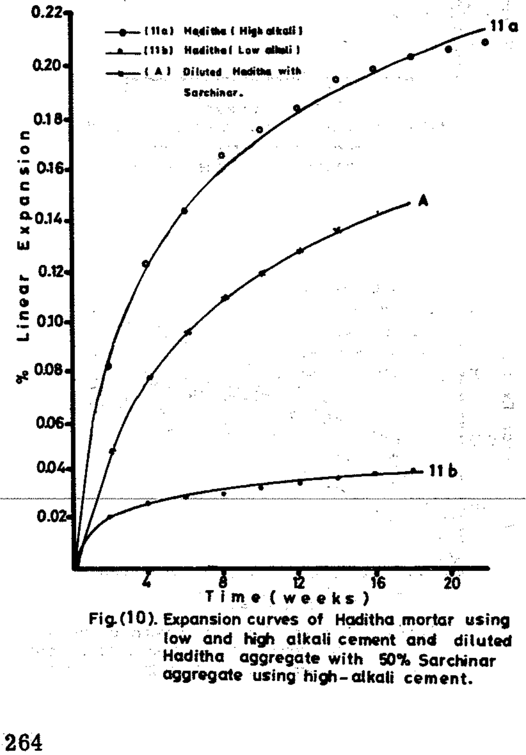

Fig.(10). Expansion curves of Haditha mortar using low and high alkali cement and diluted Haditha aggregate with 50% Sarchinar aggregate using high-alkali cement.

Results of Rock Cylinder Test:

The percent linear expansion data of rock cylinders from twenty five quarries after four weeks correlated well with the fourteen week expansion data of their respective mortar bars. This suggests that the abnormal expansion of the concrete is likely to be due to the abnormal expansion of the aggregates used.

Results of the combined evaluation of the quarries:

Table (2) attempts to compare the results of the petrographic test, mortar bar test, cylinder test and the compressive strength test carried on the samples from all the investigated quarries. An overall grading system is suggested whereby a total of seven grades are distributed among the four test as follows: Three for the mortar bar test, two for the petrographic test, and one for each of the rock cylinder and compressive strength test.

The results of this evaluation can be used as an objective measure for the suitability of the carbonate rocks from Iraqi quarries for concrete aggregate uses.

Acknowledgments:

The authors would like to express their indebtness to the Building Research Centre of the National Research Foundation, and in particular to Dr. Z. A. Rauof, Dr. A. Al-Adeeb and the UNESCO senior expert Mr. Auto Berger.

The assistance and help of the Head of the Geology Department of the University of Baghdad, Dr. Y. Al-Rawi is highly acknowledged.

Table (1): Combined evaluation of the carbonate quarries.

Quarry Name		Petrographic Test		Rock-Cylinder Test	Mortar Bar Test	Compressive strength test	overall Grading	
		physical quality	chemical quality					
Shanafia	a	satisfactory	innocuous	non-expansive	non-expansive	accepted	6.4	7
	b	fair	innocuous	—				6.5
	c	poor	innocuous	—				6
Derbendikhan		satisfactory	innocuous	non-expensive	slight-expansive	accepted	6.0	
Sarchinar		satisfactory	innocuous	non-expansive	slightly-expansive	accepted	6.0	
Salah Al-Din		satisfactory	innocuous	non-expansive	slightly-expansive	accepted	6.0	
Anah (a,b)		satisfactory	innocuous	non-expansive	slightly-expansive	accepted	6.0	
Abu-Sfayya(a,b)		satisfactory	innocuous	non-expansive	slightly-expansive	accepted	6.0	
Samawa 1	a	fair	innocuous	-	slightly-expan-	accepted	5.7	5.4
	b	satisfactory	innocuous	non-expansive	slightly-expansive	accepted		6.0
Hit	a	satisfactory	innocuous	non-expansive	slightly-expansive	accepted	5.7	6.0
	b	satisfactory	innocuous	-				5.9
	c	fair	innocuous	non-expansive				5.5
	d, e	fair	innocuous	-				5.4
Dokan		fair	innocuous	non-expansive	slightly-expansive	accepted	5.5	
Wadi Msad		fair	innocuous	non-expansive	slightly-expansive	accepted	5.5	
Hammam Al-Alil		fair	innocuous	non-expansive	slightly-expansive	accepted	5.5	

Shiththatha	a,d	fair	innocuous	-	slightly-expansive	accepted	5.4	5.4
	b	poor	innocuous	-				6.0
	c	satisfactory	innocuous	non-expansive				4.9
Haiydia	a	poor	innocuous	-	non-expansive	not accepted	5.3	5.0
	b	fair	innocuous	non-expansive				5.5
Kubbaisa	a	poor	innocuous	non-expansive	slightly-expansive	accepted	5.2	5.0
	b	fair	innocuous	-				5.4
Tayarat		satisfactory	innocuous	slightly-expansive	moderately-expansive	accepted	4.9	
Wadi Swab		satisfactory	innocuous	slightly-expansive	moderately-expansive	accepted	4.9	
Khan Baghdadi	a	satisfactory	innocuous	non-expansive	moderately expansive	accepted	4.8	5.0
	b,c	satisfactory	innocuous	-				4.9
	d	fair	innocuous	non-expansive				4.5
Badosh		fair	innocuous	non-expansive	slightly-expansive	not accepted	4.5	
Rawa	a	fair	innocuous	non-expansive	slightly-expansive	not accepted	4.5	4.5
	b	fair	innocuous	-				4.5
Wadi Horan	a	satisfactory	deleterious	-	slightly-expansive	not accepted	4.3	3.9
	b	fair	innocuous					3.9
	c,e	poor	innocuous	-				4.9
	d	satisfactory	innocuous	-				4.4
Samawa 2	a	poor	innocuous	-	slightly-expansive	not accepted	4.2	3.9
	b	fair	innocuous	non-expansive				4.5

Qalat Mazlum	a	fair	innocuous	slightly expansive	-	not accepted	4.2	4.4
	b	poor	innocuous					3.9
Kilo 45		fair	innocuous	moderately-expansive	moderately expansive	accepted	4.0	
Kilo 60	a	poor	innocuous	non-expansive	slightly-expansive	not accepted	4.0	4.0
	b	poor	innocuous	-				4.0
Rutba	a	fair	innocuous	slightly-expansive	moderately expansive		3.6	4.4
	b	poor	innocuous					2.5
	c	satisfactory	deleterious	slightly-expansive				3.9
Ghussaiba	a	fair	innocuous	non-expansive	moderately expansive	not accepted	3.0	3.5
	b	poor	innocuous	-				2.5
Baiji		poor	deleterious	slightly-expansive	slightly-expansive	not accepted	2.9	
Haditha	a	fair	deleterious	expansive	expansive	not accepted	1.3	0.5
	b	fair	innocuous	non-expansive				2.5
	c	poor	innocuous	-				1.0

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Jersey

6. CASE STUDY INVESTIGATIONS

THE CHAIRMAN'S INTRODUCTION TO THE SESSION ON CASE STUDY INVESTIGATIONS

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The conference so far has been mainly concerned with laboratory studies and simulation of 'rim phenomena' on one hand, and a mix of cement production, chemical technology and early life characteristics of setting cement on the other.

This session gives us the opportunity to take the research laboratory and cement production technology approaches a significant stage further into the world of concrete construction and performance.

In practice there are many variables to handle - the local environment, the mix design, the materials, the workmanship and the techniques of concrete production. Therefore laboratory investigations inevitably suffer a little because they cannot reproduce all the full scale conditions, and case studies and field work hence form a prime tool for our applied research. There is a further important but somewhat different consideration, it is in our appreciation of economic factors and the performance of concretes in practice, where our collective image to the industry is largely portrayed.

Thus I hope this session can help bridge the gap between theory and practice.

To illustrate the complex influence of some variables, I will show you, a little light heartedly, an extreme case history (parts of which are under litigation therefore I cannot give specific details). Please treat it in the spirit in which it is given. It concerns a large industrial complex in the Middle East, in an area where the environment is hot, arid and coastal. The aggregates are a variety of igneous and carbonate rocks, that are generally weak, porous and often contaminated with evaporite salts. The environment, the materials and certain aspects of the workmanship and design has led to many deficiencies in the performance of the local concrete in the short and medium term. The longer term problem of expansive alkali silica and perhaps alkali carbonate reactions, which are also present, tend to pale into insignificance as the effective life of the concrete is often finished before serious damage to concrete from alkali reaction becomes significant.

Fig. 1 shows in simplified form the relationship of alkali reaction problems compared in time with the other principal problems found. The photographs show some of the defective concrete, cracks and other deterioration which has occurred due to a variety of causes acting singly and in combination e.g. plastic shrinkage, plastic settlement, shrinkage cracking, cracks related to reinforcement corrosion, cracks due to thermal movement, shear and tensile stress cracks due to design inadequacies, internal and external chemical sulphate attack and physical salt weathering.

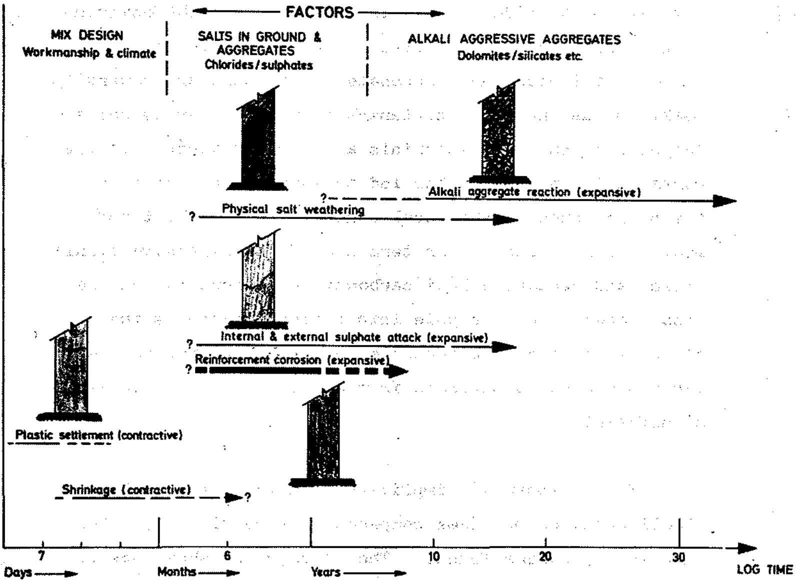
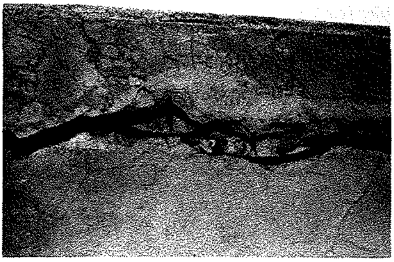
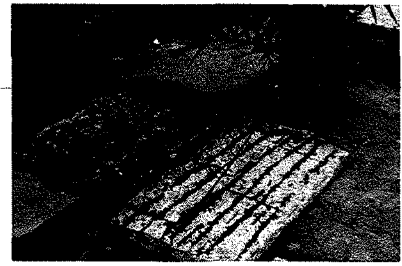
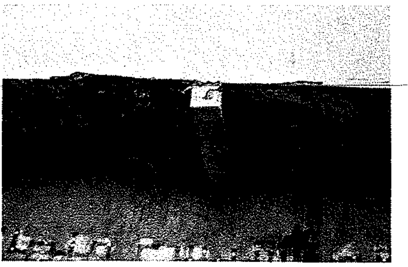

FACTORS
MIX DESIGN
Workmanship & climate
SALTS IN GROUND & AGGREGATES
Chlorides/sulphates
ALKALI AGGRESSIVE AGGREGATES
Dolomites/silicates etc.
? Alkali aggregate reaction (expansive)
? Physical salt weathering
? Internal & external sulphate attack (expansive)
? Reinforcement corrosion (expansive)
Plastic settlement (contractive)
Shrinkage (contractive) ?
7
6
10
20
30
Days
Months
Years
LOG TIME

Fig. 1







INFLUENCES ON THE ALKALI-AGGREGATE REACTION UNDER FIELD CONDITIONS

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Introduction

Up to 1965 the generally held view in Germany was that there was in this country no alkali-aggregate reaction causing severe damage to concrete. Although in a few instances alkali-aggregate reaction was considered as a possible cause of cracking and scaling on concrete constructions in north Germany, this was done more in view of relevant findings in the neighbouring country of Denmark. Usually the deterioration was mostly seen as the result of other causes, such as frost action and excessively high stress due to shrinkage or temperature. This until then widely accepted view about a possible deleterious alkali-aggregate reaction changed when in 1968 near Lübeck a bridge had to be pulled down, because its stability could no longer be guaranteed. In 1974 a further bridge was for the same reason closed to traffic and replaced by a new one. After 1968 there were more frequent reports about cases of concrete deterioration due to alkali-aggregate reaction in north Germany, and even trivial damage resulting from all kinds of causes was often attributed to deleterious alkali-aggregate reaction. This is hardly surprising, since damage due to alkali-aggregate reaction can easily be confused with damage which has in fact been caused by frost or other expansive reactions.

To get some idea of the possible risk alkali-aggregate reaction may constitute to concrete constructions in Germany, extensive tests were performed. Because of the complex nature of the alkali-aggregate reaction and the numerous influential factors, a great number of aspects had to be considered, such as the influence of type, quantity and grain size of the aggregate as well as that of the alkali content. This involved short-time tests on normally small specimens under severe conditions. S. Sprung already reported on some of these tests at the last symposium at Reykjavik. But short-time and simplified tests alone do not yield sufficiently reliable information if it has not first been established whether these findings can safely be applied to the behaviour of corresponding concrete units. It was with this in mind that over the last 8 years extensive concrete tests and investigations into the behaviour of constructions have been carried out at our institute.

The research into the behaviour of constructions was necessary because concrete tests in laboratories naturally do not cover all practical construction factors, such as concrete production under field conditions, the influence of the dimensions of the building units, loading and stress conditions of the reinforcement and design details.

The concrete tests I am going to speak about were compared with the structural behaviour of concrete constructions which had been erected in north Germany several years - in some cases even decades - previously and for which aggregate of this area had been used. The publication by Bonzel and Dahms on alkali-aggregate reaction in concrete /¯1_7, of which you all received a copy, is mainly concerned with these studies.

Concrete Tests, Composition, Storage

The composition of the concretes was such that in addition to concretes of different strength and density also the direct influence of the concrete composition, such as differences in the effective alkali content of the concrete as well as quantity and size range of the alkali-reactive aggregates, could be investigated. We therefore used for the testing concretes with equal cement content and different water-cement ratio as well as those with equal effective alkali content, but different Na_2O-equivalent of cement and relevant cement content. The water-cement ratio ranged from 0.40 to 0.70, the cement content from 300 to 600 kg/m^3.

The primary storage conditions were storage in the open, that is exposure to the normal weather conditions, wet storage at 40 °C and 100 % relative humidity (fog-chamber) and dry storage at 20 °C and 65 % relative humidity. To study in addition the influence of the dimensions of the specimens, concrete beams measuring 10 cm x 10 cm x 50 cm and 10 cm and 30 cm sized cubes were made for the various tests.

As evidences of deterioration we registered gel precipitation, efflorescence, scaling and cracking on cubes and beams and differently large longitudinal expansions of beams stored in the fog-chamber. Especially when studying parameters, about which little is known, the assessment of the alkali-aggregate reaction solely on the basis of expansions, as one frequently finds in the literature, is not sufficient. The dimensions too may affect the deterioration. For example, no expansions or only very small ones could be found on beams and yet the 30 cm sized cubes showed quite substantial cracks and precipitations of alkali silicate gel. We therefore used - as table 1 illustrates - for the assessment of the degree of deterioration a classification of five stages, whereby 0 for instance means no expansions and cracks and 3 some bigger cracks, which would also in practice be described as more severe damage. Group 5 covers very severe cracking and expansions over 3 mm/m. For each of the three types of storage the most unfavourable deterioration degree was determined.

TABLE 1: Assessment of Damage

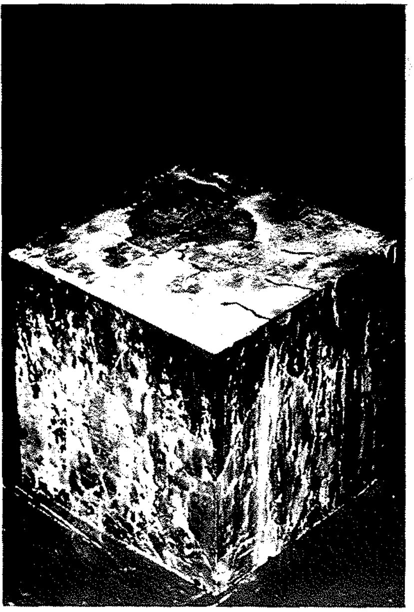
Degree of damage	Damage to beams or cubes stored in the open or in the fog-chamber	Expansions in mm/m of beams stored in the fog-chamber+)
0	no cracks	up to 0.3
1	some isolated fine cracks	0.3 to 0.5
2	several fine cracks	0.5 to 0.8
3	some bigger cracks (with a width over 0.2 mm), also some fine cracks	0.8 to 1.5
4	several bigger and fine cracks	1.5 to 3
5	very severe cracking on all surfaces	>3

+) including an expansion of approximately 0.2 mm/m due to a temperature increase from 20 to 40 °C

Test Results

a) Influence of Moisture

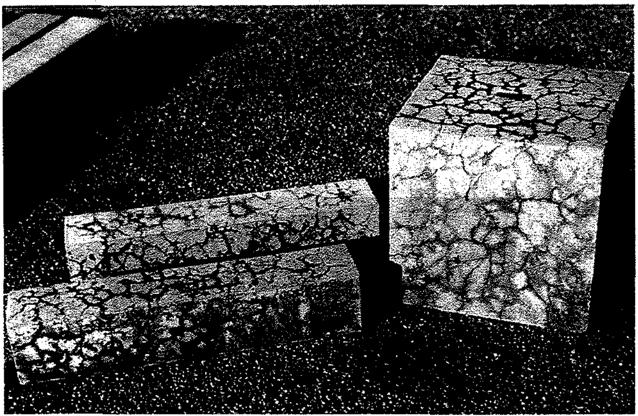
When concretes of an unfavourable composition were tested which over several years had been exposed to different storage conditions, first evidences of a deleterious alkali-aggregate reaction could be found during storage in the fog-chamber and at temperatures of 40 °C two to four weeks after the start of the wet storage. As time passed this damage increased to reach its climax at concrete ages of 6 months to one year at the latest (Fig. 1).



Deleterious alkali-aggregate reaction on a 30 cm sized cube stored in the fog-chamber (damage degree 5)

FIG. 1

With a storage in the open, that is an unrestricted exposure to the weather, the damage on similarly composed concretes reached the same extent, only a little later (Fig. 2). These results are in line with findings on constructions in north Germany as regards their environmental conditions.



Deleterious alkali-aggregate reaction on beams
and 30 cm sized cubes stored in the open (degree 5)

FIG. 2

To find out in how far the inherent moisture of massive concrete constructions even in dry surroundings is responsible for the occurrence of a deleterious alkali-aggregate reaction, specimens were immediately on demoulding wrapped in foil. After three months they were unwrapped and the deterioration seen in Fig. 3 became apparent, consisting mainly of damage to the surface in the form of precipitations and a few fine cracks. It must therefore be concluded that in massive constructions the inherent moisture may suffice to cause a certain amount of damage. This problem needs to be studied further.

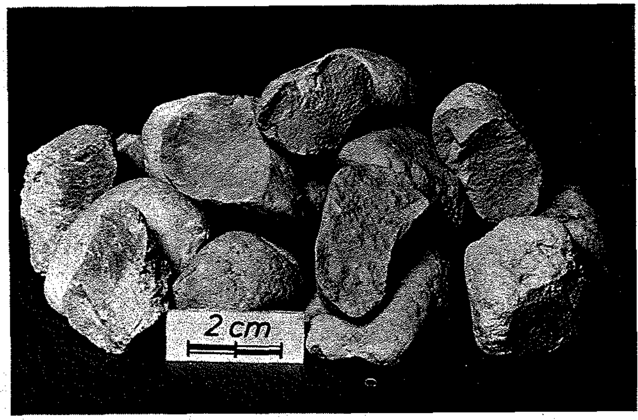
b) Influence of the Aggregate and the Granulometric Composition

In north Germany occurs as alkali-reactive aggregate opaline

Deleterious alkali-aggregate reaction on a 30 cm sized cube which has immediately on demoulding been wrapped in foil

FIG. 3

sandstone (Fig. 4) and to a lesser extent reactive flint. As a consequence of various tests we today assess the alkali-reactivity of concrete aggregate on the basis of its contents of opaline sandstone and reactive flint (see also recommendations). As table 2 shows it is distinguished between "safe", "conditionally useful" and "critical" aggregates.



Opaline sandstone

FIG. 4

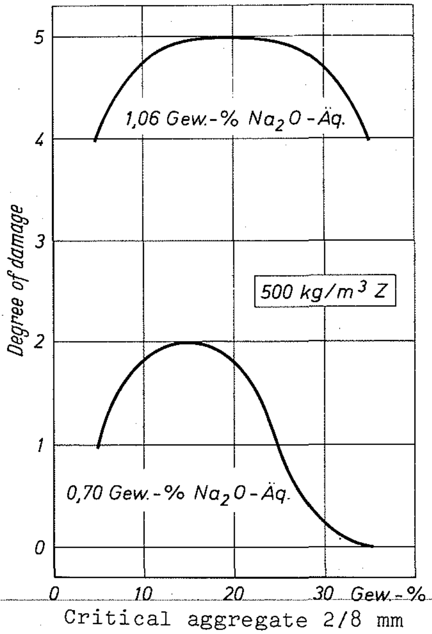
TABLE 2: Assessment of Aggregate with alkali-reactive Constituents

Constituents	Limit values in % by weight for the reactivity groups		
	safe	conditionally useful	critical
opaline sandstone + other opal-containing rocks[+)] over 1 mm	<0.5	0.5 to 2.0	> 2.0
reactive flint over 4 mm	<3.0	3.0 to 10.0	>10.0
5 x (opaline sandstone + other opal-containing rocks) + reactive flint	<4.0	4.0 to 15.0	>15.0

+) including reactive flint 1 to 4 mm

If the aggregates contained as critical constituents opaline sandstone, it was under adverse conditions possible to produce damage, no matter whether size range 0/32 mm or only size range 4/32 mm consisted of critical aggregate. But under otherwise equal conditions the highest degree of damage was reached when size range 2/8 mm contained critical aggregate and the remaining aggregate was made up of useful material.

The content of the alkali-reactive aggregate in the size range 2/8 mm was also found to be of considerable significance. In Fig. 5 the degree of the damage to the concrete due to alkali-aggregate reaction has been plotted versus the amount of the alkali-reactive aggregate in the size range 2/8 mm. The highest degree of damage was mostly reached for the concrete with approximately 15 to 25 % by weight of alkali-reactive aggregate in the size range 2/8 mm, based on the total amount of aggregate.



Degree of damage to concrete due to alkali-aggregate reaction versus the amount of the alkali-reactive aggregate in the size range 2/8 mm

FIG. 5

With a few further tests we also studied the performance of a similar concrete which contained no alkali-reactive aggregate of the size range 2/8 mm, that means only the remaining aggregate up to 32 mm was alkali-reactive. Here we merely obtained damage up to degree 2 instead of degree 5 when the size range 2/8 mm consisted of alkali-reactive aggregate.

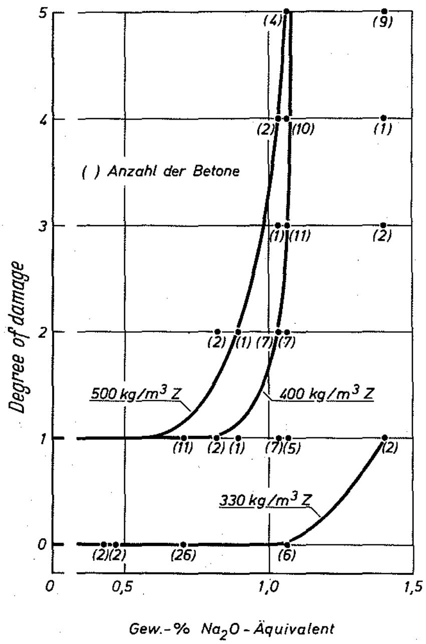
c) Influence of the Cement and the Cement Content

The effective alkali content in the concrete results from the effective alkali content of the cement and the cement content per m^3 concrete. Although both factors may determine the total alkali content in the concrete, they cannot be evaluated exactly in the same way. The cement content also affects the properties of the concrete, such as strength, density, texture and deformation behaviour. The alkali content of the cement, on the other hand, hardly changes these concrete characteristics at all. So far our tests have shown that for both parameters there is a certain threshold value, above which damage may occur and that the influence of the alkali content of the cement is of somewhat greater importance than that of the cement content. Fig. 6 demonstrates this behaviour for concrete with a water-cement ratio of 0.45. Only alkali contents over 0.9 led to a more marked deterioration, that is damage exceeding degree 2. At the same time, the cement content was in these cases always at least 400 kg/m^3, with higher water-cement ratios at least 350 kg/m^3.

Some preliminary tests (Fig. 7) on concretes of cements with Na_2O-equivalents of over 1 and of cement contents slightly under 400 kg/m^3 produced damage above degree 2 when the water-cement ratio exceeded 0.55. But these initial tests are to be followed up by further investigations.

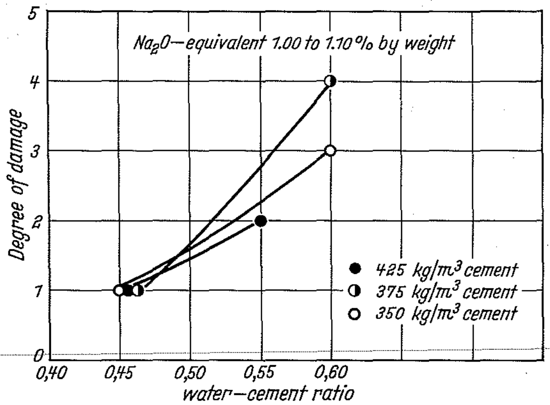
Conclusions

On the basis of the tests carried out at our institute and the investigations into the behaviour of concrete constructions the following can be said: A deleterious alkali-aggregate reaction could only be found on concretes of an unfavourable composition when the specimens had been subjected to wet storage or on



Degree of damage to concrete due to alkali-aggregate reaction versus the effective alikali-content of the concrete

FIG. 6



Influence of the water-cement ratio on alkali-aggregate reaction

FIG. 7

concrete constructions in wet environmental conditions. However, tests on concrete samples whose drying process had been inhibited also showed that in massive constructions the moisture inherent in the concrete is sufficient to cause deleterious alkali-aggregate reaction.

The degree of damage was mainly dependent on the composition of the total aggregate. As especially unfavourable were those which contained very alkali-reactive aggregate in an amount of approximately 15 to 25 % by weight of the total aggregate in the size range 2/8 mm.

Marked deterioration occurred on wet stored concrete specimens with very alkali-reactive aggregate ("critical") when the cement content in the case of a cement with an effective alkali content of approximately 0.90 % by weight Na_2O-equivalent was 500 kg/m^3 and in the case of a cement with an effective alkali content of approximately 1 % by weight Na_2O-equivalent 400 kg/m^3. In general, the damage increased with higher water-cement ratios.

When the deterioration as a result of alkali-aggregate reaction was assessed, it became clear that this damage on concrete constructions can easily be confused with damage due to other causes. For the study of unknown aspects of the alkali-aggregate reaction it is not enough to measure the expansions of the specimens when their behaviour is to be investigated, it is in fact also necessary to consider the deterioration on other specimens, for instance 30 cm sized cubes.

On the basis of the present state of knowledge the precautionary measures set out in table 3 were recommended in Germany as being on the safe side.

TABLE 3: Precautionary Measures against deleterious Alkali-Aggregate Reaction in Concrete

Alkali-reactivity of the aggregate	Environmental conditions		
	dry	wet	wet + alkali supply from outside
safe	none	none	none
conditionally useful	none	low-alkali cement[1]	low-alkali cement
critical	none	low-alkali cement	exchange of aggregate[2]

[1] only with concrete of the strength classes Bn 350 and higher

[2] only with concrete of the strength classes Bn 350 and higher, otherwise low-alkali cement

References

1. J. Bonzel and J. Dahms, beton 23, 495 and 547 (1973).

CONTRIBUTIONS TO DISCUSSION

Dr. D. Hirche

I wish to comment on the statement of B. Mather and Dolor-Mantuani "the reactive part of flint is the $CaCO_3$ - SiO_2 impurity in flint or the leached $CaCO_3$":

1) There are no reactive parts in the flint. IR spectroscopy of fine grains shows that flint has very large numbers of silica groups like opal or pyrex glass. This is because of the high proportion of lattice defects all over the flint grains. We shall suggest that alkalies can react with the whole grain.

2) Alkali reactions start on the outer surface of a silica grain because there are more defects arising from crystal growth or from the crushing process. However, the reaction occurs on internal interfaces too.

REPORT ON REACTIVE CONCRETE AGGREGATE FROM THE CAPE PENINSULA, SOUTH AFRICA

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ABSTRACT

Several concrete structures in the Cape Peninsula show serious cracking and deterioration due to dimensional change. The common factor in all the structures has been found to be the coarse aggregate, commonly known as Malmesbury shale or Malmesbury hornstone. The deterioration apparently occurs both where low-alkali and high-alkali cements have been used. X-ray data were obtained for the reaction product in the concrete but attempts to index it were unsuccessful. The main reaction product produced in the laboratory by adding saturated lime water to Malmesbury shale could, however, be indexed and was found to agree closely with calcium silico-aluminate (7).

Introduction

In South Africa the existence of a serious and widespread problem arising from the excessive shrinkage of concretes and mortars containing certain Karroo aggregates was first demonstrated by Stutterheim (1) in 1954. He concluded that the general cracking pattern observed in reinforced concrete structures could only be explained on the basis of excessive shrinkage and expansion of the concretes. Although it was at this stage known that alkali-aggregate reaction could cause expansion, it was concluded from both field and laboratory evidence that expansion was not the cause of deterioration. Detailed investigations subsequently carried out by Roper (2) led to the conclusion that problems encountered with the dimensionally unstable Karroo aggregates were due to shrinkage.

In 1971, during an investigation of aggregate generally known as Malmesbury shale or Malmesbury hornstone intended for use in concrete for a proposed civic centre in Cape Town, the NBRI expressed concern about the possibility of this type of aggregate being dimensionally unstable in the presence of calcium, magnesium and sodium ions. The investigation revealed that the aggregate contained illite and that the potassium of the illite could be quite easily replaced by magnesium, calcium and sodium, resulting in a vermiculite type of mineral.

Oberholster and Brandt (3) in 1974 examined concrete from a structure in Cape Town that showed serious cracking and found signs of cement-aggregate reaction which resembled alkali-aggregate reaction. Malmesbury shale was used as the coarse aggregate.

Incidence of Problem

Following on the above finding of cement-aggregate reaction in a concrete structure which showed distress, the NBRI was informed of several other structures which displayed similar signs of deterioration. These structures were visited and examined.

No attempt was made to conduct a systematic survey to determine the number of structures showing the same type of cracking. Eleven bridges and one dam, which showed the same pattern of cracking, were examined. In addition, a concrete road was also beginning to show signs of deterioration that could be associated with cement-aggregate reaction.

The following is a brief description of some of the structures that were inspected and of the concrete of which samples are being investigated in the laboratory.

The Steenbras Dam

The original Steenbras Dam (4) was a gravity concrete structure consisting of a curved portion and two straight flanks, in which precast concrete blocks were used as forms. The extreme length of the wall was 428 m and the length of the spillway 67 m. It was completed in 1921.

During the early 1950s it was decided to strengthen the existing dam and raise it by 1,8 m. In essence the process was one of placing vertical cables through the wall of the existing dam from the crest into the foundation and stressing the cables to produce stabilizing compressive forces on the upstream face. Construction of the raised portion was completed in 1954.

Table Mountain sandstone was used as coarse aggregate for the original dam while Malmesbury shale coarse aggregate was used for the 457 mm-thick raised section.

Recent inspection has revealed deterioration of the components associated with the heightening of the wall. The raised portion of the wall is leaning forward by an amount varying from 16 mm in 1 m to 42 mm in 1 m (5). Cracks, similar to those shown in Figure 1, were seen in the southern wing wall and other tie heads. The 100 mm-thick reinforced walkway slabs are under considerable compression; it is not clear whether this is due to dimensional change of the walkways or to dimensional change of the tie heads on which they rest.

FIG. 1
Cracking in right flank terminal tie head, Steenbras Dam

Pirow Street Bridge

Construction of the Pirow Street Bridge took place between February and July 1961. The piers, transoms, longitudinal beams and deck were all cast in situ. The coarse aggregate used was Malmesbury shale, the fine aggregate Cape Flats sand and the cement was one with a low alkali content, i.e. less than 0,60 per cent alkali calculated as Na_2O. Cracking of the transom beams became noticeable in 1965 and the bridge deteriorated to such an extent that remedial action had to be taken only nine years after its completion. Figure 2 shows the cracks in the end of a transom beam. It is important to note that the stringer (longitudinal) beams of two adjacent spans rest on the transom beam and that water from the deck finds its way down between the joints of the deck and the stringers and collects on the surface of the transom beam.

FIG. 2

South-west end of transom beam showing serious cracking, Pirow Street Bridge

N2 National Road

The N2 concrete road was opened in 1971. The coarse aggregate used was Malmesbury shale while Cape Flats sand with a shell content of about 28 per cent was used as fine aggregate. A high alkali cement was used. A cursory examination of the road surface revealed fine cracks. However, it is not clear whether this is due to expansion or shrinkage.

Foot of conductor mast

Cores of the concrete from the foot of a conductor mast are also being examined in the laboratory. The concrete displayed severe cracking which appeared to be due to expansion. Malmesbury shale coarse aggregate was used.

Factors common to all the structures that were inspected and which displayed cracking are that they contain Malmesbury shale coarse aggregate, the cements used had either a low alkali or a high alkali content and obvious cracking was usually observed about five years after completion of the structures.

Appearance of the Concrete

Hand specimens of pieces of the concrete and of concrete cores have a characteristic appearance on freshly fractured surfaces.

The general impression is that there is a dark reaction rim, 0,5 to 1 mm wide, around the periphery of the aggregate. Closer inspection, however, reveals that a white reaction product occurs as a deposit on the fracture surfaces. The deposit is thickest 0,5 to 1 mm away from the periphery, forming a distinct white ring 1 to 1,5 mm wide around the inside of the periphery, decreasing abruptly to approximately a uniform thickness over the rest of the surface (see Figure 3). It appears that the reaction product has been drawn by capillary action into cracks in the aggregate.

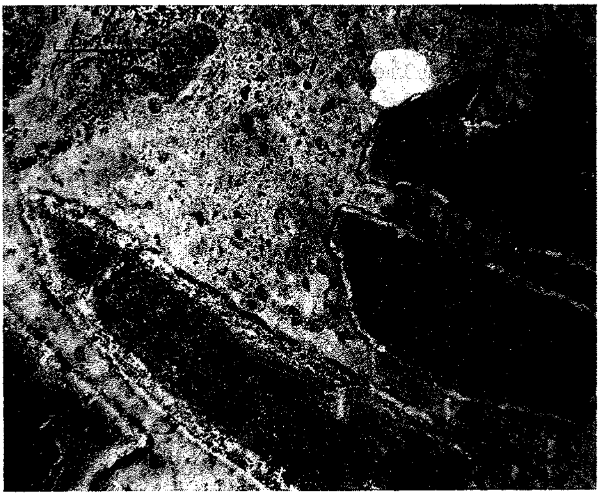

FIG. 3

White deposit of reaction product occurring on fracture surface of coarse aggregate. Concrete from foot of conductor mast

White deposits are also seen filling voids in the mortar, occurring on the impression surfaces of aggregate on the mortar and also on the surfaces of aggregates, where the aggregate and mortar have broken away from each other.

Malmesbury Shale Aggregate

The coarse aggregate in Cape Town generally known as Malmesbury shale or Malmesbury hornstone in the main consists of spotted hornfels, argillaceous quartzite, feldspathic quartzite, phyllite and baked shale.

There are nine quarries producing some 2,4 x 10^6 m^3 of this type of aggregate annually. The aggregate produced by the various quarries can differ greatly in mineralogical composition and physical properties. Even in the same quarry there can be extreme variations as shown by the data in Table 1, which shows the chemical composition of aggregate collected from three different quarries.

TABLE 1

Chemical Composition of Malmesbury Shales

Sample No	Chemical Composition (%)							
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	H_2O^+
E1	72,66	13,36	3,34	1,53	1,30	3,38	3,04	0,75
E2	57,39	20,92	7,09	4,16	1,13	2,36	3,86	2,64
E3	57,86	21,32	7,05	4,05	1,21	2,19	3,89	2,73
E4	59,27	19,88	6,50	3,95	1,70	2,74	4,05	2,66
E5	73,73	13,17	3,20	1,40	1,41	2,77	2,67	1,22
E6	74,05	13,08	3,23	1,40	1,32	2,85	2,27	0,98
B1	70,62	15,06	3,71	1,89	0,87	3,04	2,49	1,21
B2	66,66	16,76	4,89	2,59	1,68	2,49	3,28	1,34
B3	61,07	19,59	6,24	3,52	1,33	2,18	3,80	1,77
T3	64,64	17,74	5,03	2,70	1,71	2,97	3,18	1,37
P1	64,80	17,05	4,92	2,69	1,11	2,78	3,23	1,68

E1 : argillaceous quartzite
E2 : spotted hornfels
E3 : spotted hornfels
E4 : spotted hornfels
E5 : feldspathic quartzite
E6 : argillaceous quartzite
B1 : argillaceous quartzite
B2 : spotted cordierite hornfels
B3 : argillaceous quartzite
T3 : run of quarry aggregate
P1 : run of quarry aggregate from E

A characteristic feature of the Malmesbury shales is the presence of illite which gives a peak on the X-ray diffractometer trace at approximately 10,1 Å. After treatment with calcium containing solution, the height of the illite peak is greatly reduced and new or stronger peaks appear at approximately 14,9 Å and 7,2 Å (see Figure 4).

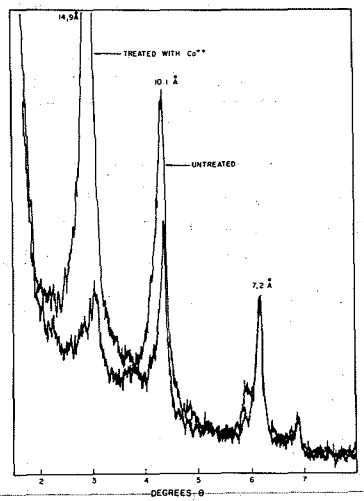

FIG. 4
X-ray diffraction trace of < 2 µm fraction
of Malmesbury shale, untreated and treated

Davis (6) estimates that 90 per cent of the coarse aggregate used for concrete in Cape Town is Malmesbury shale. As the shale does not readily crush to a good cubical particle shape, the particle shape quality of the aggregate produced by most of the crushers in the Cape Peninsula varies from poor to fair.

Fine Aggregate

The fine aggregate used in most of the concrete in Cape Town is known as Cape Flats dune sand. In the past this sometimes contained shell and sometimes was free of shell. However, almost the only dune sand now being used for concrete contains 25-30 per cent shell. The sand has a narrow grading, 95 per cent being in the fractions between 1 180 and 150 µm (6).

Cements

Ordinary portland cements from three factories are being used in the Cape Peninsula. Two of these are high-alkali cements and one is a low-alkali cement. The chemical analyses of the three cements are given in Table 2.

TABLE 2

Chemical Composition of Cements

Cement No	Chemical Composition, %									
	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	SO_3	loi*
a	20,58	4,92	3,52	0,09	0,97	63,60	0,27	0,55	2,77	0,85
b	20,58	5,19	3,56	0,10	1,31	62,96	0,21	0,88	2,57	1,23
c	20,45	5,05	2,22	0,05	1,10	63,22	0,21	0,27	2,75	2,46

* loi = loss on ignition

Laboratory Investigations

Examination of concrete

Figure 5 shows a polished specimen of concrete from the Pirow Street Bridge as seen under reflected light. A reaction product occurring between the contact of the aggregate and the mortar has a gel-like appearance and shows desiccation cracks. Figure 6 is a scanning electron micrograph of this reaction product.

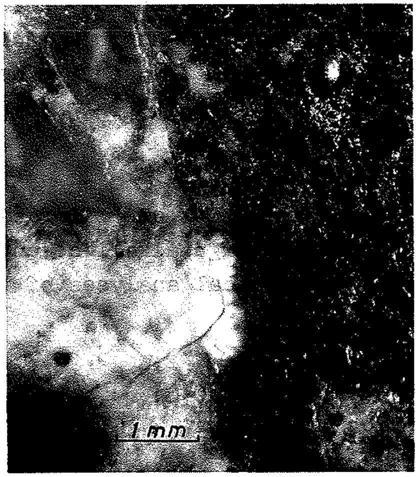

FIG. 5

Photomicrograph of concrete from Pirow Street Bridge showing reaction product

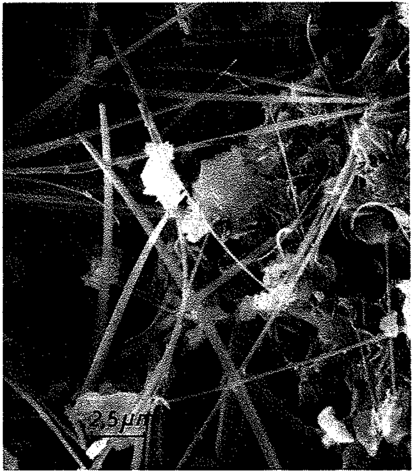

FIG. 6

Scanning electron micrograph of reaction product, Pirow Street Bridge

Reactivity of Malmesbury Shale

Based on the premise that the illite in the shale could react with calcium ions of the portland cement as follows

$$\text{K-illite } (10\ \text{Å}) + \tfrac{1}{2}\,\text{Ca}^{++} \longrightarrow \text{Ca-vermiculite } (14\ \text{Å}) + \text{K}^{+}$$

thus releasing potassium ions which would be available for alkali-aggregate reaction, ASTM test C 227-71 was carried out on two Malmesbury shales and a quartzite control aggregate, using a low-alkali cement from the Transvaal. The maximum linear expansion recorded after nine months was 0,027 per cent, the average for the control being 0,022 per cent.

Results of the same test repeated with Malmesbury shale and the two high-alkali and one low-alkali cement from the Cape are still inconclusive. The results for the control of Pyrex glass with the same cements gave values of 0,041 per cent for cement a, 0,060 per cent for cement b and 0,011 per cent for cement c after four weeks.

Of nine Malmesbury shales tested for potential reactivity by the chemical method ASTM C 289-71 five were shown to be potentially deleterious. All the hornfelses, except one, were shown to be innocuous, while all the argillaceous and felspathic quartzites, except one, were shown to be deleterious by the chemical method.

Malmesbury shales were put in stoppered conical flasks with saturated lime water at 22°C. In time a white gel appeared. <u>All</u> the samples shown to be innocuous by ASTM test C 289-71 produced the reaction product within three days after the addition of lime water while all the samples shown to be deleterious by the test produced the reaction product only after 19 days. The amount of reaction product increases with time. Almost no reaction product is produced at 38°C, and a fair amount at 10°C.

Water extracts of cements a, b and c (Table 2) were prepared and added to the Malmesbury shale aggregate E2. A reaction product appeared first with the extract of cement c and the amount produced after six weeks was more than twice the amount produced with the extracts of cements a and b.

Reaction product

Examination with the SEM of the reaction product produced by adding saturated lime water to Malmesbury shale showed a mat of long slender fibres occurring together with a gel-like mass (Figure 7). Calcium carbonate and an occasional perfectly developed crystal resembling hydrogarnet were also present.

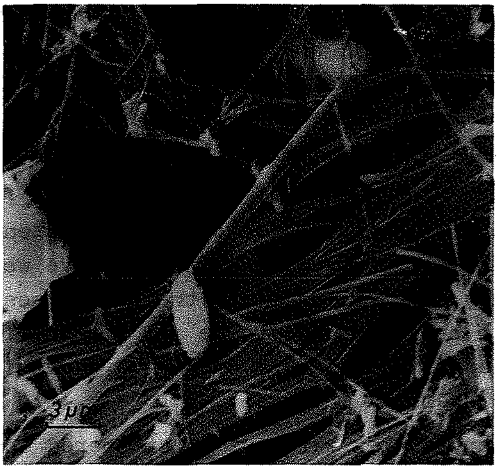

FIG. 7

Scanning electron micrograph of reaction product of Malmesbury shale with $Ca(OH)_2$

X-ray diffraction analysis done on the reaction product of Malmesbury shale with saturated lime water gave values that agreed fairly well with the values reported by Carlson and Berman (7) for calcium silicoaluminate. The reaction product in the concrete gave d-values that varied from structure to structure, the only resemblance being that in all the samples d-values of 9,4 Å and higher are recorded. The results for the reaction product of Malmesbury shale with saturated lime water are compared with the values given for calcium silicoaluminate by Carlson and Berman in Table 3.

TABLE 3

X-ray diffraction values of reaction product and calcium silicoaluminate (7)

1		2	
dÅ	Relative intensity	dÅ	Relative intensity
9,58	100	9,69	100
5,54	20	5,56	25
4,91	18	4,94	10
4,65	18	4,68	8
3,85	41	3,85	14
3,57	12	3,57	6
3,45	15	3,44	14
3,19	18	3,20	6
3,01	12	3,00	4
-	-	2,88	10
2,77	5	2,77	8
2,74	16	2,74	10
2,67	5	2,66	6
2,58	6	2,58	10
2,54	45	2,54	16
2,18	18	2,157	4
2,13	10	2,130	8

1 : Malmesbury shale + saturated lime water
2 : Calcium silicoaluminate (7)

Conclusions

The cracking observed in the Cape Peninsula for structures built with concrete containing Malmesbury shale as coarse aggregate has not so far been simulated in the laboratory. No expansion of mortar bars made with Malmesbury shale and either low-alkali or high-alkali cements and tested in accordance with ASTM C 227-71 was observed. The ASTM C 289-71 chemical test for reactivity yielded anomalous results in the case of Malmesbury shale.

A reaction product was observed in all the affected structures. In all instances X-ray diffraction data give high d-values for the product. It could not be proved that the reaction product is the cause of the deterioration of the concrete.

A gelatinous reaction product is produced when saturated lime water is added to Malmesbury shale. X-ray diffraction data for the crystalline component agree closely with the values reported by Carlson and Berman (7) for calcium silicoaluminate.

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TENTATIVE PROGRAMME OF INVESTIGATION TO PREVENT CEMENT-AGGREGATE REACTION OCCURRING IN HARDENED CONCRETE

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ABSTRACT

"Map-cracking", followed by disruptive expansion, is occurring in a few concrete structures in the Cape Area. It is associated with abnormally wet conditions and a particular type of coarse aggregate, which appears to react with $Ca(OH)_2$ liberated from hardened cement. It is thought that it may be possible to prevent this reaction by incorporating a pozzolanic material in the cement. A series of exploratory tests are described, and a programme for further investigation is suggested.

THE PROBLEM

Abnormal cracking of concrete at several localities in the Cape Peninsula and Western Cape area has been observed during the past 5 to 10 years. This specific phenomonem ("map-cracking") in concrete about 3-5 years old seems to occur only under the particular condition where moisture is present either continuously or frequently. Dr. Oberholster (1) and Mr. Flanagan (2) will have described the problem fully by now.

In the course of his investigations, at the National Building Research Institute, Dr. Oberholster found that a reaction occurred between lime water and a sample of Malmesbury Shale (frequently used for coarse aggregate) in his possession. The reaction product had an appearance similar to an alminium-hydroxide precipitate.

Although our Company has no direct interest in the manufacture or use of coarse aggregate or concrete, as the major manufacturers of cement in the area the management of the Cape Portland Cement Company felt that we should interest ourselves in this problem and see whether we could do anything to alleviate it.

POSSIBLE SOLUTIONS

We previously manufactured a Marine cement containing a pozzolan (calcined shale), and one of the main functions of this pozzolan was to react with the calcium-hydroxide set free during the hydration of the portland cement portion of the "Cemarine", rendering it insoluble, so reducing the ultimate porosity of concrete structures and, inter alia, adding to their ultimate strength.

It seemed logical, therefore, to carry out tests in an attempt to determine whether calcined shale, in finely divided form, in concrete, would tend to react with liberated calcium-hydroxide BEFORE this material could react with the coarse aggregate, and so prevent the disruptive expansion which has occurred in some concrete structures, as mentioned above, An alternative solution, of course, may be to incorporate finely ground Malmesbury Shale in the concrete.

As full scale "in situ" tests would obviously take years to yield results, we gave consideration to devising some form of test method which would at least give an indication of the efficacy, or otherwise of the proposed remedial measures.

EXPERIMENTAL PROCEDURE

An "extract" of the soluble hydration products (mainly calcium hydroxide) of cement was made by shaking 10 grams of cement with 100 ml water, in a closed vessel in an automatic shaker, for seven days. This gave the cement a reasonable time to hydrate, and kept the reaction products in intimate contact with the water. The mixture was then filtered, and the clear filtrate kept in a tightly stoppered vessel.

Similar extracts were made using two ordinary portland cements (one "high" and one "low" alkali) and one sulphate resisting cement (low alkali).

These extracts were then placed in 250 ml rubber-stopped erlenmeyer flasks, together with 50 grams of coarse aggregate (crushed to minus half-inch size). In some cases finely ground calcined shale was added as well. The flasks were shaken for a few minutes, then allowed to stand undisturbed in a constant temperature room (22 to 25°C), and observed weekly.

TABLE 1

Details of experiments set up

No.	Date	Aggregate		Calc. Shale gm.	Liquid	
		Wt. gm.	Type		ml	Type
0	April'76	300	D.H. Limestone	-	300	$Ca(OH)_2$ sat.soln.
1	"	300	Malmesbury shale	-	300	" " "
2	May '76	±100	Dolomitic	-	±100	" " "
3	"	±200	Granitic	-	±200	" " "
4	"	±100	Dolomitic	-	±100	" " "
5	4.6.76	50	Malmesbury shale	-	100	Ext.OPC high alk.
6	"	50	" "	0,5	100	" " "
7	"	50	" "	2,5	100	" " "
8	"	50	" "	-	100	Ext.SRC low alk.
9	"	50	" "	0,5	100	" " "
10	"	50	" "	2,5	100	" " "
15	2.7.76	50	" "	-	100	Ext.OPC low alk.
16	"	50	" "	0,5	100	" " "
17	"	50	" "	2,5	100	" " "
18	July'76	±850	" "	-	±850	$Ca(OH)_2$ sat.soln.

Numbers 11 and 14 were mixtures of 5 gm OPC, 25 gm M. shale and 100 ml water. Numbers 12 and 13 were the same, but with added calcined shale. The mixtures were shaken for a week and then allowed to stand. It is impossible to see whether reactions are occurring or not.

OBSERVATIONS

In table 2 below the symbols have the following meanings with regard to visible reaction (or lack of it):

- \- Definite negative
- 0 Uncertain
- \+ Definite positive

TABLE 2

Observations recorded weekly

Number	Observation for week ending:									
	11/6	18/6	25/6	2/7	9/7	16/7	23/7	30/7	6/8	13/8
0	-	-	-	-	-	-	-	-	-	-
1	+	+	+	+	+	+	+	+	+	+
2									-	-
3									+	+
4									-	-
5	-	0	+	+	+	+	+	+	+	+
6	-	-	-	-	-	-	-	-	0	0
7	-	-	-	-	-	-	-	-	0	0
8	-	0	+	+	+	+	+	+	+	+
9	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-
15					-	0	+	+	+	+
16					-	-	-	-	-	-
17					-	-	-	-	-	-
18*					+	+	+	+	+	+

* Reaction showed up after 4 days

The positive reactions between the limewater/cement extracts and the Malmesbury shale show up quite definitely after 3 to 4 weeks and can be clearly seen on colour slides and colour photographs. (The reaction with the granite sample took over two months to show up and is still mild compared with that of the Malmesbury shale). Where the powdered pozzolan is present it is not really possible to say that there is definitely no reaction occurring because of the "masking" effect of the powder. There is certainly no "floc" floating around in the supernatant liquid, as is the case in numbers 5, 8, 15 and 18 (this can also be seen on the slides and photos). Hopefully the $Ca(OH)_2$ is reacting with the calcined shale instead of with the Malmesbury shale. At any rate the reaction appears to be independent of the alkali content of the cement.

FUTURE PROGRAMME

It is suggested that future tests should be based on the ASTM C227 test for potential alkali reactivity of cement-aggregate combinations (mortar-bar method) - an expansion test.

The test will have to be modified, however, to use concrete specimens instead of mortar bars, and similar bars will have to be stored under different conditions, e.g. one lot in air (dry), a second lot in a high humidity cupboard, a third lot under water, and a fourth lot subjected to alternate wetting and drying cycles.

Each of the above lots will need to be made up with "pure" cements and with cements containing varying proportions of calcined shale and varying proportions of finely ground Malmesbury shale. It will probably be worthwhile trying a few samples in the autoclave to see whether it is possible to speed up the reaction, but any results obtained would have to be treated with considerable reserve until such time as long-term results were available for confirmation.

References:

(1) Session IV Dr. R.E. Oberholster, C.S.I.R., South Africa, "Report of reactive concrete aggregate from the Cape Peninsula South Africa".

(2) Session IV Mr. J. Flanagan, P.C.I., South Africa, (Cement-aggregate reactivity problems in South Africa).

REVIEW OF UP TO DATE INVESTIGATIONS OF ALKALI REACTION IN CONCRETE WITH AGGREGATES FROM BASIC SOURCES IN SOME REGIONS OF YUGOSLAVIA

N. Pandurović and V. Dučić*

Although the alkali-aggregate reaction phenomena have been known for more than thirty five years, first investigations in this direction have been carried out in Yugoslavia as late as 1960 year. To the necessity of testing materials for possible alkali-aggregate reaction first pointed out Institute for Testing Materials in Beograd, during preliminary testings of concrete and concrete components, which had to be used for building a large gravitational dam on the river Drina**.

By these preliminary investigations has been established that cements which were available for this object had an alkali content of more than 0.6 % and, by the mineralogical analysis of perspective aggregates from sources closest to the object, has been found that the percentage of chert in different fractions of aggregates is from 2 % to 11.5 % (Table 1).

Table 1

Fraction,	Chert content, percents		
mm	Excavation site 1	Excavation site 2	Excavation site 3
2-8	9.3	2.4	5.2
8-16	11.5	10.4	5.2
16-63	6.8	2.6	2.0
63-150	0	0	0

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* Institute for Testing materials, Beograd, Vojvode Mišića 43.

** Drina is the major tributary of the river Sava, with the lenght of more than 300 km and with the river basin area of about 20,000 km^2.

Data presented had shown that further investigations,to prove wether an alkali-aggregate reaction is taking place, should proceed.

Investigations which were carried out are as follows:

1. Testing of alkali reactivity of chert by a fast chemical method, according to ASTM C 289-58 T.

2. Investigation of cherts structure by X - ray difraction method.

3. Testing of chert activity, according to the Yugoslav standard B.C 1.018 (Standard for testing activity of pozzolan).

4. Investigation of chert activity, by the accelerated method of cement resistance to sulphate corrosion testing (Method I.I. Karpinski *).

First two testing methods are common procedures to identify harmfull ingredients in an aggregate which could possibly produce tne alkali-aggregate reaction. Investigations by 3 and 4 were not used for identification of alkali-aggregate reaction before, but it have been chosen as additional proofs fo the possible chert reactivity.

Investigations by the method 3 were carried out by making mortar probes with grinded chert (separated from the aggregate) and comparing its compressive and flexural strenghts with strenghts of corresponding probes made with grinded quartz sand and grinded pozzolan opaline breccia. All these materials were grinded and sieved to the fineness better than 90 μ .

Results of this test are given in the Table 2.

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* Karpinski I. I. Augmentation de la resistance à la corrosion du micro-beton par la substitution limitèe calcaire dans le granulat quartzeux. - Revue des materiaux No. 568 (1963).

Table 2

Series of probes	Compressive strenght kp/cm^2	Flexural strenght kp/cm^2
R	0	0
K	0	0
OB	172	41.5

R - Mixture of grinded chert with hydrated lime and standard sand.

K - Mixture of grinded quartz sand with hydrated lime and standard sand.

OB - Mixture of grinded pozzolan opaline breccia with hydrated lime and standard sand.

Investigations by the method 4 were carried out by comparative measurements of weight loss of mortar prismes (4x4x16 cm). Test probes were subjected to cyclic submersions into the saturated solution of Na_2SO_4 and drying periods on 30°C and 50 % relative humidity. Four series of probes were prepared. All probes were made of mortar 1:3 (cement:standard sand) and with W/C = 0,50.

- Series KT

  Portland cement with 25 % of cement substituted by grinded quartz sand.

- Series KU

  Portland cement with 25 % of cement substituted by grinded chert (separated from an aggregate).

- Series KW

  Pozzolanic cement (the same Portland cement as for other series with 30 % opaline breccia). 25 % of cement substituted by grinded quartz sand.

- Series KX

  Pozzolanic cement with 25 % of cement substituted by the grinded chert.

All probes were cured for 28 days in water before the actual testing. Mechanical characteristics tested were after 28 days as follows in the Table 3.

Results of accelerated corrosion tests are given in diagrames 1 and 2.

Table 3

Series of probes	Compressive strenght kp/cm^2	Flexural strenght kp/cm^2
KT	238	39.3
KU	237	38.3
KW	204	35.6
KX	210	41.3

On the basis of all methods presented has been concluded:

- The aggregate is not reactive according to the first method (ASTM C 289-58 T). This, by results obtained by other autors, is not allways corresponding to the real behaviour of the aggregate in concrete and it can be inconsistent with results of the other testing methods.
- Investigations by the X - ray difraction are showing the crystal structure of chert, which correspond to the α - quartz.
- The finely grinded chert is not showing any activity, based on activity tests, and its behaviour is the same as that of the pure quartz sand grinded to the same fineness in composition with the hydrated lime, while control experiments with the pozzolan opaline breccia are showing an activity corresponding to the 170 kp/cm^2 compressive strenght of probes.
- The same conclusion can be obtained on the basis of testings by the method 4. From tests results could be established that the series KU, in which 25 % of the cement was substituted with the finely grinded chert, had not shown any retarding effect to the deterioration of probes in the agressive solution compared to the series KT, with 25% of grinded quartz sand. This conclusion is valid also for series KW and KX.

Since all conclusions are consistent, it was established that the aggregate from the river Drina basin is not reactive.

Few years after these initial investigations started broader testings of aggregates from Drina basin, both upstream and downstream from the dam mentioned. These testings, although not performed in a small scale, are still not completely systematic. However, results gave sutable data about reactivities or nonreactivities of aggregates obtained from various locations along the river. Besides the other points, it has been demonstrated that aggregates from various deposits close to the mouth of Drina and downstream from the dam mentioned are potentialy reactive, so that an aggregate from this region should be tested before its use as a concrete component.

In the future, during the next few years, investigations about reactivity of gravel and silicate aggregates along the river Drina will be completed and systematized to obtain complete survey of aggregates behaviour from the Drina basin.

Some incomplete and local investigations of aggregates reactivities were performed in various parts of Yugoslavia, in much smaller scale. Systematic investigations started two years ago, with aggregates from the river Velika Morava* and along the whole river basin of Velika Morava. These investigations are proceeding and will be completed in few more years.

Investigations were proposed and programmed by Institute for Testing materials, which is carrying out the whole programm. Investigations are including testings of very numerous samples of aggregates from many separations along the Morava basin. Aggregates, which are of the silicate origin, are subjected to complex testings, including mineralogical investigations, investigations by the chemical ASTM method, investigations on mortar probes and, in the further phase, testings on larger concrete specimens. Together with laboratory testings will be investigated behaviour of concrete objects, which in the past were builded with aggregates from the same origin and which are subjected to conditions favorable for the development of alkali-silicate aggregate reaction in concrete.

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* Velika Morava is a Danube tributary, with the lenght of 215 km and with a river basin of 36,000 km^2.

It has to be stated that up to date, in Yugoslavia were not observed any damages, due to alkali-silicate aggregate reaction, in concrete objects.

First results of complex investigations of aggregates from Velika Morava basin are indicating that it is a potentially reactive material. If it will be confirmed during the further investigations and so if aggregates are reactive wihout doubt, it will be necessary to prevent alkali-aggregate reaction in concrete objects builded with such aggregates. It will be a very difficult task, since Velika Morava basin is one of the basic sources of aggregate in this part of Yugoslavia and up to now its use in concrete objects building was quite successfull.

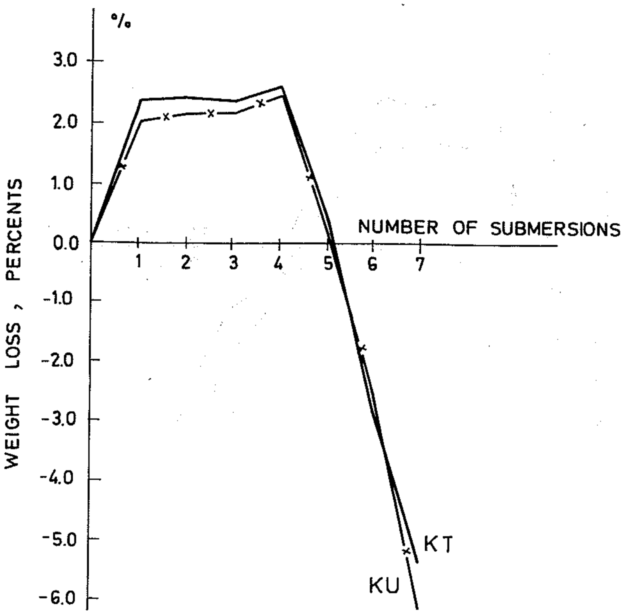
%
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
WEIGHT LOSS , PERCENTS
NUMBER OF SUBMERSIONS
1
2
3
4
5
6
7
KT
KU

DIAGRAM 1

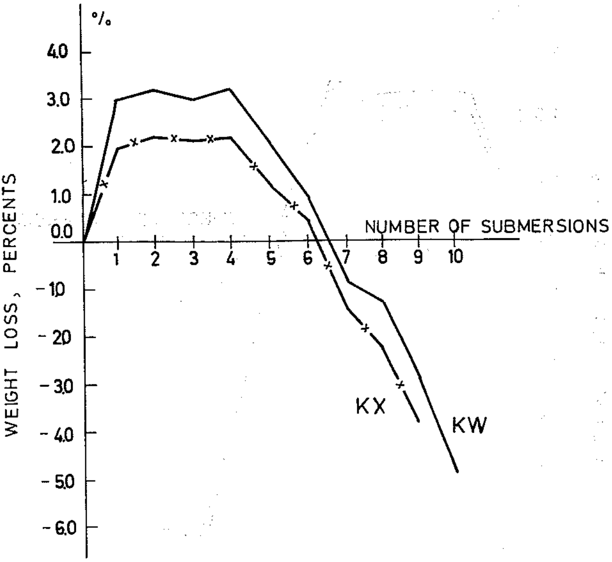
%
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
WEIGHT LOSS, PERCENTS
NUMBER OF SUBMERSIONS
1
2
3
4
5
6
7
8
9
10
KX
KW

DIAGRAM 2

EXPANSION OF CONCRETE CONTAINING NEW ZEALAND ARGILLITE AGGREGATE

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and

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SUMMARY

The expansive behaviour of concrete containing (a) Matahina greywacke-argillite (0.04% in 12 years) and (b) a lightweight aggregate produced by heat treatment of Oxford argillite (0.13% in 5.5 years) is described. The reaction mechanism for the expansion of concrete containing Matahina greywacke-argillite is still not known. An alkali-silica reaction is unlikely to have been the cause of the expansion as both pozzolan and low alkali cement were used and no sign of alkali-silica reaction was found by petrographic examination. Calcium oxide was identified in the fired Oxford argillite, but the expansive reaction due to the rehydration of this calcium oxide is unusual because of its small grain size and low concentration in the fired aggregate.

INTRODUCTION

The expansion of concrete due to alkali-aggregate reaction has been found to be caused by a reaction between the alkalis present in cement and certain types of siliceous minerals giving rise to the formation of expansive alkali-silica gels. This reaction was extensively reviewed by Bredsdorff et al(1) and many other investigations have been reported since. More recently, another type of alkali-aggregate reaction has been described which appears to involve the interaction of the cement alkalis with some of the clays present in greywackes, argillites and phyllites, causing a slow but steady expansive reaction which in some cases has continued for over thirty years.(2,3)

The clays identified to date are interlayered vermiculite chlorite and possibly montmorillonite. It has been suggested that the cement alkalis remove interlayer cementing precipitates of alumina and silica from these clays allowing chemisorption of water on the newly formed surfaces with resultant swelling pressures. Generally the reaction has been characterised by the absence of alkali-silica gel, but where this has been present it has been attributed to being derived from the interlayer silica. Tests have indicated that the expansive reaction is suppressed by the addition of pozzolanic material to the concrete.(2)

Recently, in New Zealand, two cases of expansive reactions in concrete involving a mixed greywacke-argillite aggregate from Matahina and a fired lightweight argillite from Oxford became apparent. Preliminary investigations indicated that, in both cases, alkali-clay reactions might be involved. This paper reports the result of investigations on these two aggregates and attempts to relate the reactions to those already described.

AGGREGATES

(a) Matahina Greywacke-argillite

Prior to the construction of the Matahina hydro project, located on the Rangitaiki River, Bay of Plenty, the durability of the local greywacke was questioned. Breakdown of the aggregate in stock-piles was noted and ascribed to the presence of significant proportions of argillite. As a result of investigations it was recommended that Matahina greywacke should not be used in any concrete subject to exposure, especially face concrete, but its use in mass concrete should be satisfactory. Matahina greywacke was used for the main structure which is of earth core design.

As part of the above investigations, concrete test specimens were prepared using Matahina greywacke-argillite and Hutt Valley greywacke a material of long proven performance, to a mix design specified by the Ministry of Works and Development. Some of these specimens were retained on an outdoor exposure site to determine their long term durability. The details of the concrete mixes used are given in Table 1.

TABLE 1

Details of Concrete Mixes used with Matahina and Hutt Valley Greywackes and Results of Exposure Tests

Sample	15A	17A
Aggregate	Matahina	Hutt Valley
Cement + pozzolan (kg/m^3)	410	410
Pozzolan (% replacement of cement	12.5	12.5
W/C+P	0.50	0.50
Air content (%)	2.8	3.3
Slump (mm)	18	28
Date mixed	30/1/63	31/1/63
Length change (% in 12 years)	+0.04	-0.01

The cement used was an ordinary Portland type with 0.32% Na_2O equivalent alkali contant and the pozzolan Whirinaki diatamaceous pumicite. The beams, 75 x 75 x 290mm in dimension, were cast and cured in 100% r.h. for seven days at 21C and then transferred to the outdoor exposure site.(4)

The Hutt Valley greywacke is a good example of the New Zealand greywacke which is widely used as an aggregate and has been described by Kennerley and St. John.(4) The Matahina greywacke is similar but differs in some details. The aggregate contains about 10% of argillite (which is usually absent from good grade greywacke aggregates) and approximately 5% of rhyolite, ignimbrite and pumice are present. The siltstone to sandstone grades of the greywacke show typical texture and are composed predominantly of quartz feldspars, scattered tiny mica flakes and tiny chips of fine grained volcanic rock and argillite. The greywacke contains rare irregular veinlets of white encrustations of laumontite. Some of the greywacke fragments are a yellow brown colour and possibly have been derived from weathered terrace gravels. The argillite fragments are smaller in size than the greywacke, less hard and often easily broken by hand. Mineralogically, the argillite is similar to the greywacke but contains a higher proportion of clay minerals. The above description of Matahina greywacke is a private communication from W.A. Watters, Chief Petrologist, N.Z. Geological Survey.

(b) Fired Oxford Argillite

The large deposit of argillite located in the Ashley Gorge, near Oxford in the Canterbury Province, has been investigated and found suitable as a raw material for the manufacture of an expanded lightweight aggregate.(5) Tests showed that another large deposit of argillite located behind the Wellington Patent Slip was also suitable and the results for this material are included for the purposes of comparison.(5) As these two deposits appeared to have good potential as raw materials for commercial production, quantities of expanded lightweight argillite were produced in a pilot rotary kiln at 1150C and a full range of concrete tests carried out. Details of mixes are shown in Table 2, and specimens were placed on the outdoor exposure site to determine their long term durability.

TABLE 2

Details of concrete mixes and results of exposure of expanded argillite specimens[a]

Bar No.	Aggr. C.A.	Source F.A.	Cement content (K/gm^3)	W/C$^+$	Slump (mm)	Unit Weight (Kg/m^3)	Age (yrs)	Length change (%)	Carb.* area (%)	Carb.* Depth (mm)	Cracking*
F8/1/2	Ox.	Ox.	260	1.1	0	1120	5.5	-0.014	67	12	Nil
F8/1/1	"	"	290	1.1	50	-	"	+0.014	54	8	Mod.
F8/1/3	"	"	350	0.83	25	1215	"	+0.044	28	4	Slight
F8/1/4	"	"	435	0.67	68	1275	"	+0.088	12	2	Slight
F8/1/6	"	"	450	0.60	0	1340	"	+0.071	10	2	Mod.
F8/1/5	"	"	530	0.60	0	1445	"	+0.060	5	1	Mod.
F8/1/7	"	"	560	0.56	87	1415	"	+0.126	8	1	Severe
F8/1/12	H.V.	Ox.	330	0.93	25	1675	"	+0.037	55	7	Mod.
F8/1/13	Ox.	H.V.	360	0.63	43	1635	"	-0.028	5	1	Nil
F10/4	P.S.	P.S.	350	0.92	62	1345	6.3	-0.020	51	8	Nil
F10/9	"	"	540	0.56	87	1560	5.7	+0.009	5	1	Mod.

+ W/C includes total water in mix.

Ox. = fired Oxford argillite

P.S.= fired Patent Slip argillite

* Based on measurements from thin section

H.V. = Hutt Valley greywacke (dense)

a. The 50 x 50 x 300 beams were cured 7 days in fog at 21C and then placed on the exposure site

Large deposits of argillite are not common in New Zealand as most argillite is interstratified with the greywacke. The Patent Slip argillite is a slightly metamorphosed, indurated, pale green-grey claystone with some chert pods. The Oxford argillite is slightly finer grained in texture and blue black in colour. Both argillites show incipient foliation.

EFFECTS OF LONG TERM EXPOSURE

(a) Matahina greywacke - argillite. For the first two years the specimens containing Matahina greywacke were relatively stable, but since then they have expanded at a slow rate, until at the end of twelve years the length change is +0.04% and still continuing undiminished. In contrast, the specimens containing the reference aggregate, Hutt Valley greywacke, contracted quickly within the first two years and the length change has now stabilised at -0.01%. Under low power stereomicroscopic examination both sets of specimens appear similar and show normal weathering and microcracking.

(b) Fired Oxford argillite. The dimensional changes of specimens containing fired Oxford argillite and some combinations with dense Hutt Valley greywacke, and also of fired Patent Slip argillite are shown in Table 2. Like the Matahina greywacke concrete these specimens were relatively stable for the first two years but once expansion started it continued undiminished. By contrast, the fired Patent Slip argillite is stable. Under low power examination the concrete beams with low cement contents are showing signs of considerable weathering while some of the beams with high cement contents cracked in half when lifted from the site for measurement.

The details and results of the petrographic examination of the concrete beams containing the above aggregates are given in the appendix.

ANALYSIS OF CLAY FRACTIONS IN AGGREGATES

Samples of greywacke and argillite were handpicked from the Matahina greywacke-argillite used for the concrete tests, crushed to pass a 52 mesh sieve and shaken for sixteen hours in water at pH 9. The minus 2 um fraction was removed by centrifuging and the fractions were analysed by powder X-ray diffraction, thermal analysis and infra red spectroscopy. Similar procedures were applied to the Oxford and Patent Slip argillites both in the raw and fired states. In addition Whites microscope test for free lime was applied to some of the fired argillites.

RESULTS OF CLAY ANALYSES

(a) Results of the analyses showed the handpicked greywacke and argillite fractions of the Matahina aggregate to be almost identical apart from some minor details. Approximately 10% and 7% of the minus 2 um fraction were recovered from the greywacke and argillite respectively. The minus 2 um fractions were principally quartz, feldspars, iron chlorite and either illite or finely divided micaceous material. The chlorite peaks were destroyed by digestion in 1 N HCl at 85C for 4 hr and many of the chlorite peaks were removed or flattened by heating at 550C. Attempts to expand the clay structures, both with 10% glycerol in water and ethylene glycol in the vapour phase at 60C, with and without Mg as the cation were unsuccessful. A typical set of XRD results are shown in figure 1. The 2 to 300 um silt fractions consisted of quartz and feldspars with some residual clays present. The above results were confirmed by thermal analysis and infrared spectroscopy.

(b) Results obtained from analysis of the Oxford and Patent Slip argillites appeared similar to that reported above. Approximately 7% of the minus 2 um fraction was recovered from each of the raw argillites. In the minus 2 um fractions (0.3% recovered) extracted from the fired argillites no clays were detected. These minus 2 um fractions contained quartz, feldspars and calcite for the fired Oxford argillite and quartz and feldspars only for the fired Patent Slip material.

No clays were detected in the minus 2 um fractions. Whites test gave a positive result for crushed, freshly fired Oxford argillite but was negative for similarly treated Patent Slip material.

DISCUSSION

(a) Matahina greywacke argillite.

No observations of the Matahina greywacke-argillite show any reason why this aggregate should have expanded in concrete. The presence of chlorite and illite or micaceous materials as the main clay constituents is typical for these types of sedimentary mesozoic New Zealand rocks. (W.A. Watters. Personal communication). Further, the expansive reaction is unusual in that not only was a low alkali cement used, but a pozzolan was also present. Thus the possibility of an alkali-silica reaction seems unlikely and this is further supported by the petrographic examinations.

There remains two other possibilities. Firstly, the degree of expansion occurring is moderate, and thus the amount of reactive rock could be small and may have been undetected in the analyses. Secondly, mineral alteration could be occurring under the moist alkaline conditions in the concrete. Some alteration of the feldspars to sericite is common in these geosynclinal greywackes though it is not clear how much of this alteration is post-depositional. This existing alteration made it impossible to determine whether any further feldspar alteration had occurred in the concrete.

Therefore at this stage it must be concluded that the expansive mechanism of Matahina greywacke-argillite is still unknown and cannot be related to the alkali-clay reactions reported by Gillott et al.(2) Neither has it been possible to associate the expansion with either the greywacke or the argillite individually. In the Matahina aggregate, greywacke predominates, but a small amount of reactive argillite could easily be responsible for the reaction. Generally, argillite is not a problem in New Zealand aggregates as quarries are chosen and worked to exclude this material because of its poor physical properties. It is only at the margins of the geosyncline that problems of argillite and marginally acceptable greywacke arises.

(b) Fired Oxford Argillite

The results of analyses of fired Oxford argillite indicate that the hydration of hard burnt lime is responsible for the expansion. Chemical analysis of the raw argillite(6) did not indicate widely disseminated calcite as being present, as the amount of calcia reported 0.50% was believed to be associated with the feldspars. Whites test on fired Oxford argillite which had been stored in open drums for five years was negative and it was not until the minus 2 um fraction from this five year old material was extracted that it was realised that calcite was probably present in the raw argillite. This is the reason why it was initially believed that unburnt clays could still be present, as Blank(7) reports their presence is one of the causes for unsoundness in fired lightweight clay aggregates.

The small amount of hard burnt lime present, estimated at less than 0.5% by XRD, has been slow to carbonate and hydrate, the fired material was not mixed in concrete until approximately one year after manufacture and expansion is still occurring in the concrete beams six years later. The expansion is associated with the fine aggregate, as the results for beams F8/1/12 and 13 clearly show, which suggests that the hard burnt lime is protected by some type of sintered or glassy coating. If this is the case the smaller particles of the fired argillite would be more reactive as there is more crushed material and thus more broken surfaces in this fraction. The fact that fired Oxford argillite is an overbloated, well sealed aggregate gives further support to this argument.

Data shown in Table 2 is confusing. If we consider the first series F8/1/1 to 7, carbonation, cracking and expansion can be related to cement content and increasing unit weight. However when we consider the other mixes reported the picture is not so clear. It is hypothesised that increasing alkali content due to increasing cement content is a factor in that sintered and glassy coatings on the hard burnt lime would be more efficiently attacked at higher cement contents. Further work is required to demonstrate this hypothesis.

CONCLUSION

In conclusion, the results suggest that the recent statement by Kennerley and St. John(4) "that no evidence has been found to suggest that the type of argillite commonly found in New Zealand would react deleteriously with cement alkalis" is no longer valid. In the case of Matahina greywacke-argillite, expansive alkali-aggregate reaction should not be possible as both low alkali cement and pozzolan were used and there should be insufficient alkalis available to initiate the reaction. Yet expansion has occurred in a manner similar to that reported for the Nova Scotia greywackes and argillites. While the underlying mechanism of the expansion in the Matahina greywacke-argillite is still unknown, the physical expansion of concrete containing this concrete is an indisputable fact. Previously, greywacke from the shallow margins of the geosyncline have not been used extensively for concrete aggregate, but their increasing use makes it imperitive that means be found for detecting potentially reactive greywackes.

In the case of the fired Oxford argillite, the cause of concrete expansion, at first suspected as an expansive clay reaction, is probably due to rehydration of lime mediated by alkaline attack on sintered or glassy coatings. It is necessary to be cautious in this conclusion. The fine grain size of the calcium oxide and its resistance to hydration is unusual. Both Blank(7) and Budnikov et al(8) state that particles of calcium oxide need to be at least approximately

5 mm in diameter to resist hydration by the water in the concrete mixer.

In both cases, discussed above, though the concrete expansions have been slow and moderate in size, they have been quite sufficient to cause damage to concrete as witnessed by breakage of specimens on the outdoor exposure site. Damage at the Matahina hydro project has not been reported to date, but investigation will be carried out to try and locate areas where greywacke may have been used inadvertently.

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APPENDIX

PETROGRAPHIC EXAMINATION OF CONCRETE SAMPLES

Matahina and Hutt Valley Aggregates

Concrete beams containing these two aggregates showed signs typical of exposure to the weather. Much fine aggregate was exposed and the surrounding cement paste was soft to a superficial depth. However most exposed particles were still firmly embedded. The original cast surfaces remained visible in a few isolated patches. Both beams were pattern-microcracked, with many of the cracks being filled with white crystalline material probably calcite. Examination of fracture surfaces in pieces broken from beams failed to reveal any reaction rims around pieces of aggregate or any other signs of deterioration apart from a few isolated microcracks.

For the purposes of microscopic examination thin sections were cut from beams 15A and 17A from the middle and near one end in each case. Drawings of the sections cut from 15A are shown in figure 2. Cracking is indicated by black lines and carbonation areas by cross hatching.

Beam 15A Containing Matahina greywacke-argillite

The cracking in figure 2 is extensive in some areas and almost absent in others. Main cracks are approximately 40 um in width with smaller cracks ranging down to 10 um. Cracks generally skirt particles of aggregate but in a number of cases run through them. General carbonation of the cement paste extends to depth of 2-3 mm around the edges and this layer is not noticeably leached. In many of the larger cracks carbonation extends to a depth of 20 mm. Considering the cracking present the limited penetration of the carbonation suggests that drying of the specimens under the exposure conditions has not at any time been extensive.

The amount of calcium hydroxide in the cement paste is consistent with the high cement content used. Leaching of the cement paste is generally absent even at carbonated edges. However, around a number of the larger aggregate particles there is a ring of cement paste in which birefringent crystals are absent suggesting a deficiency in calcium hydroxide. While this effect is somewhat haphazard it is noticeable and suggests some movement of precipitated material into the aggregate particles concerned.

The larger air voids in the concrete are only occasionally rimmed with calcium hydroxide but many of the smaller pores are completely filled with this material. Ettringite was not present in any of the pores or cracks. Generally, the hardened cement fabric is dense and sound apart from cracks and no alkali-silica gel or other reaction products were noted either in the cement paste or particles of aggregates.

The coarse aggregate is a mixture of greywacke, sandwacke and argillite. The fine-grained matrix of the rock is variable and complex and appears to consist of a mixture of quartz, and feldspars in a highly birefringent fine-grained mass of mica flakes together with tiny chips of volcanic rocks and argillite. Laumontite and prehnite were present in some particles as vein material but not in significant quantities. The fine aggregate is similar to the coarse aggregate but individual pieces tend to be more homogeneous. There is a significant proportion of acid volcanic rocks present, such as rhyolite, ignimbrite, rhyolitic pumice and even a few pieces of andesite. The larger fragments of the aggregate are often rounded and appear water worn. Many of these pieces are cracked and weathered and physically these fragments cannot be considered suitable for high grade concrete. It was not possible to distinguish any signs of alteration in the fine-grained matrix of the greywacke or argillite due to possible reaction with the cement.

Beam 17A Containing Hutt Valley greywacke

The cracking and carbonation is outlined in figure 3. There is less cracking than in beam 15A and it is of a different character. Most of the cracks are shorter and do not extend far into the fabric of the concrete. Where cracks are present in the interior they are mainly discontinuous and much narrower than those present in beam 15A. Apart from this, the general state of the hardened cement paste is similar to beam 15A except that the band of paste deficient in calcium hydroxide surrounding many aggregate particles is much less pronounced.

The aggregate is a typical example of Hutt Valley greywacke. It is more homogeneous than the Matahina greywacke in the sense that the fabric does not seem to be as complex or such a mixture of size ranges and the micaceous material is not as noticeable. Argillite is rare and the only volcanic rocks present are spillites. Prehnite is present as vein material but laumontite was not noted. In general, the aggregate is more compact, and less weathered than that from Matahina.

Fired Oxford and Patent Slip Argillites

The surfaces of the beams with low cement contents were soft with little aggregate exposed. Pattern microcracking was visible on the surface of the beams from F8/1/3 to 7 and displacement of these cracks was evident in beams F8/1/6 and 7, where some discolouration of crack edges occurred. Many of the cracks were filled with calcite. Examination of fracture surfaces in pieces broken from the beams did not reveal the presence of any rims around aggregate particles or any other signs of deleterious reactions. The same trends were found with beams F8/1/12 and 13 and F10/4 and 9.

Beams F8/1/1 to 7 Containing fired Oxford argillite.

The cracking and carbonation is shown in figure 4. There is a marked change in the texture of the hardened cement fabric of these beams as the cement content increases. At the lowest cement content, carbonation is intense and leaching is apparent but cracking is almost absent. Weathering and carbonation is sufficiently severe to have weakened the fabric and many of the larger particles of aggregate have been penetrated by carbonation products. In beam F8/1/3 carbonation is more normal and less leached. At the higher cement contents the hardened cement fabric is typical of dense concrete and penetration of aggregates by carbonation products is absent. However cracking in these samples is severe both in the cement fabric and also in many fragments of aggregate. The transition zone between carbonated and uncarbonated cement paste is abrupt even in the most intensely carbonated beams. Around many of the larger fragments of aggregates the zone of cement paste deficient in birefringent crystals was noted suggesting a movement of calcium hydroxide into the aggregate particles concerned.

The fired Oxford argillite is heavily overbloated and there are numerous very large pores separated by thin septums of highly frothed glass. The outer rims of the fired aggregates are brown and well sealed where the original surface is intact. Numerous minute birefringent crystals are present scattered through the glassy matrix of the aggregate fragments. These crystals were too small to be positively identified but generally appeared to be quartz and feldspars.

Beams F8/1/12 and 13 Containing mixtures of fired Oxford argillite and dense Hutt Valley greywacke.

The cracking and carbonation is shown in figure 5. The concrete in beam F8/1/12 appears similar to beam F8/1/3 or 4 in degree of carbonation and cracking. The replacement of the fired coarse aggregate by dense Hutt Valley greywacke has had little effect. In contrast, where the fired fine aggregate has been replaced in beam F8/1/13 the effect is dramatic. The concrete now has all the appearance of a normal dense concrete interspersed with lumps of fired argillite. This beam has weathered extremely well.

Beams F10/4 and 9 Containing fired Patent Slip argillite

Cracking and carbonation are shown in figure 6. Both these beams showed the same trends as the F8 series. The degree of cracking in beam F10/9 appears greater than warranted by the expansion of 0.009%, but cracks are much narrower than for beam F8/1/5.

The fired Patent Slip argillite is denser and not as heavily bloated as the fired Oxford argillite. Some foliation is present and more unbloated particles were noted. Penetration of carbonated products into rims of aggregate particles was absent.

CAPTIONS TO FIGURES

Fig. 1 Typical X-ray diffraction patterns of Matahina argillite.

a. K saturated

b. Mg saturated sprayed with 10% glycerol in water.

c. K saturated and heated 550 C/4hr.

d. No cation. Digested in 1N HCl for 4hr/85C

X-radiation Cu Ka Carbon monochrometer used.
Scan rate $\frac{1}{2}$°/min sensitivity 200 c.p.s.
Time constant 4 sec. Scale factor 1

Fig. 2 Outline drawing of thin sections of Matahina greywacke-argillite showing cracking and carbonation. Cross hatching delineates carbonation. End and middle sections. 75 x 75mm sections.

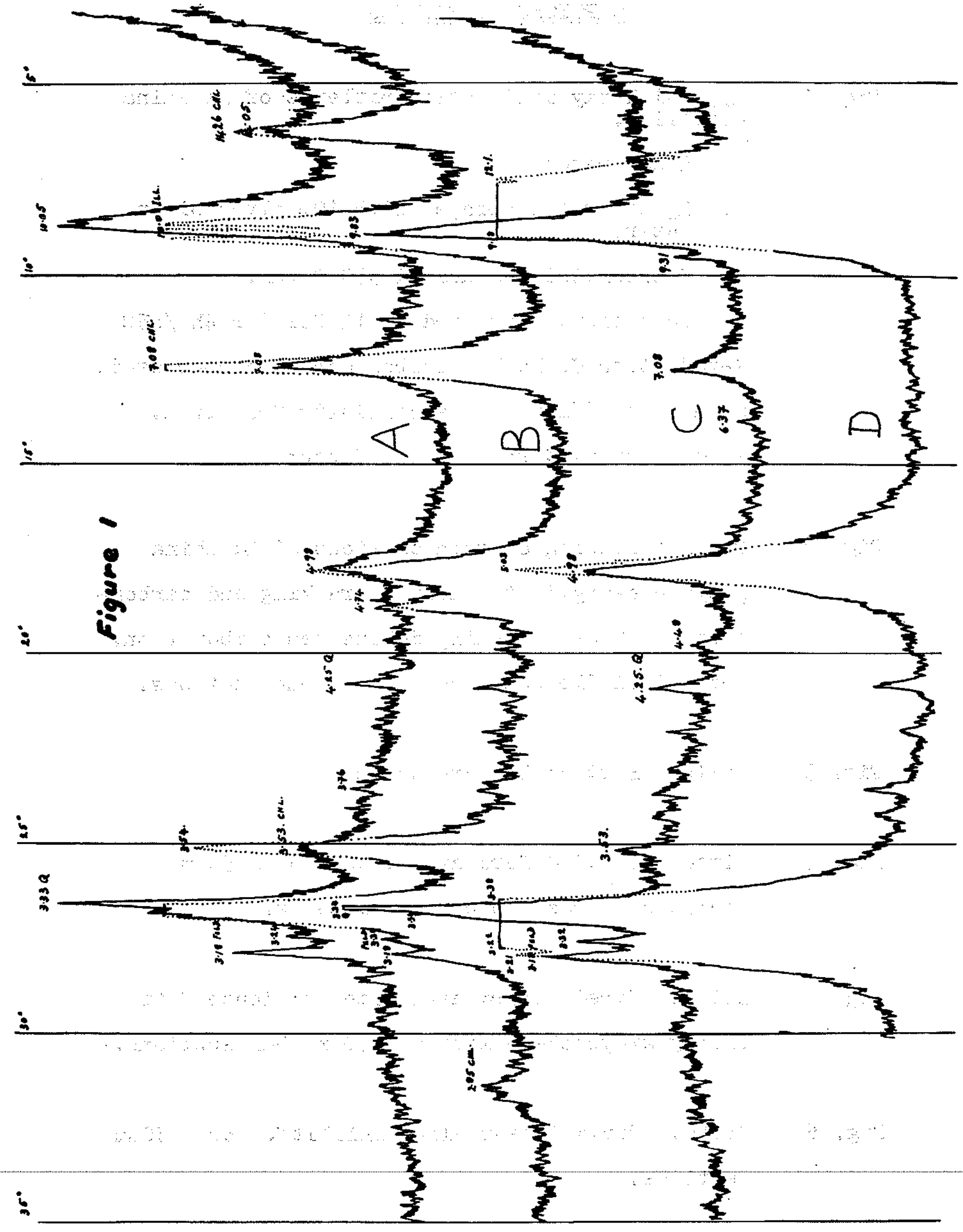
Fig. 3 Ditto. Hutt Valley greywacke

Fig. 4 Ditto. Fired Oxford argillite. 50 x 50mm sections. See table 2 for details.

Fig. 5 Ditto. Fired Oxford argillite and dense Hutt Valley greywacke mixtures. 50 x 50mm sections.

Fig. 6 Ditto. Fired Patent Slip argillite. 50 x 50mm sections.

Figure 1


5°
10°
15°
20°
25°
30°
35°
A
B
C
D
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14.05
11.05
10.0 ILL.
9.83
12.1
9.8
9.31
7.08 CHL.
7.08
7.08
6.37
4.99
5.03
4.98
4.74
4.25 Q
4.25 Q
4.49
3.76
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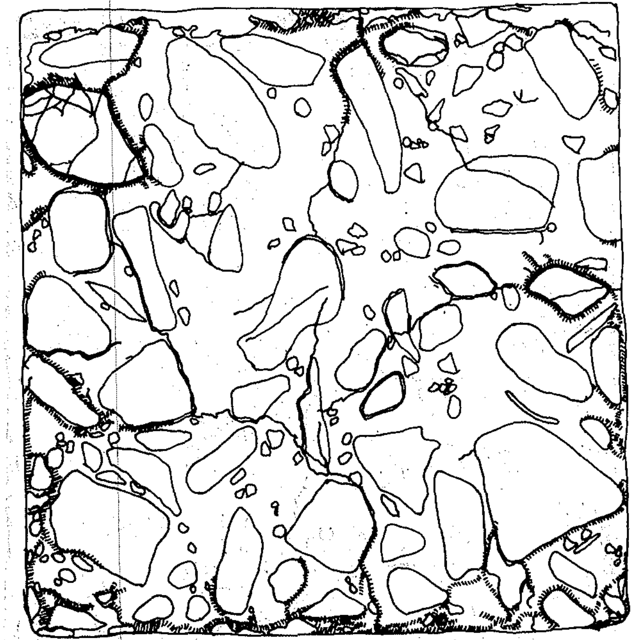
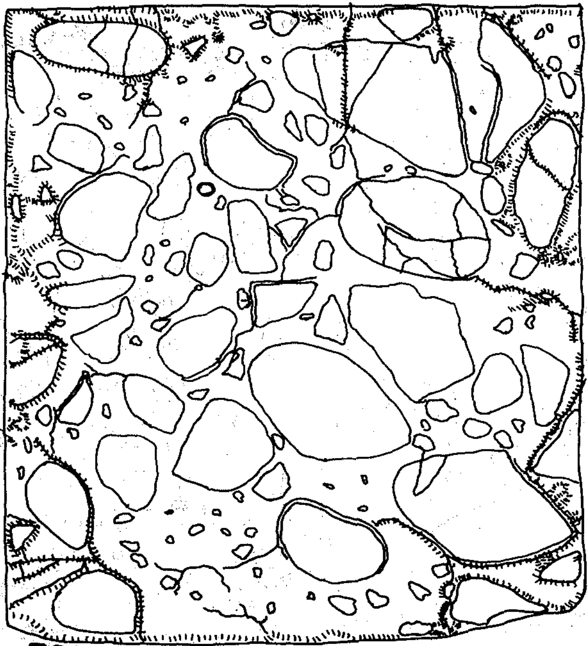
3.21
3.22
2.95 CHL.



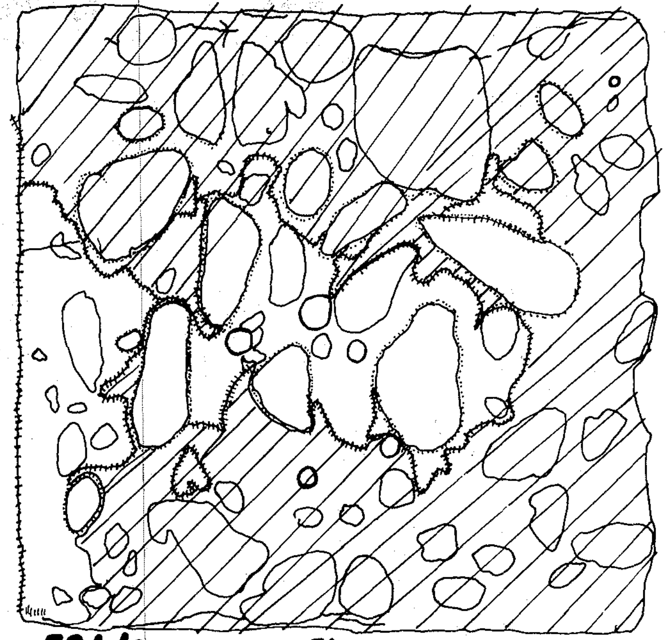
ISA-M Fig. 2.



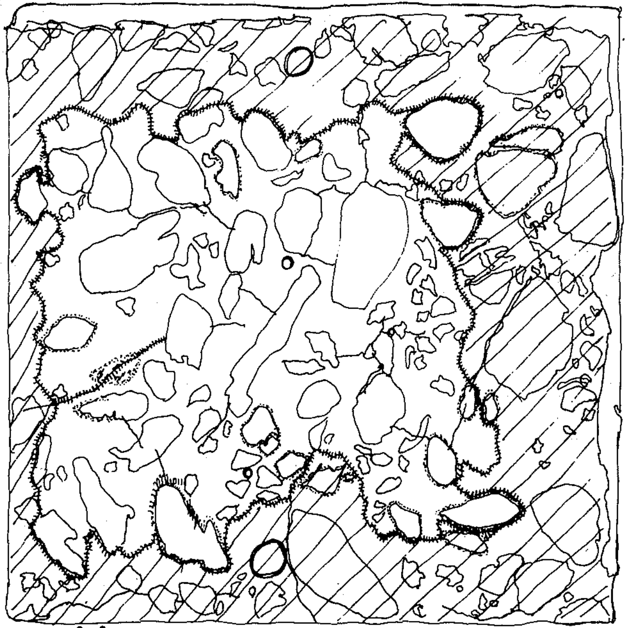
ISA-E Fig. 2.

I7A-M Fig. 3.

I7A-E Fig. 3



F8/1/2 Fig. 4



F8/1/1 Fig. 4

Fig. 4 F8/I/4

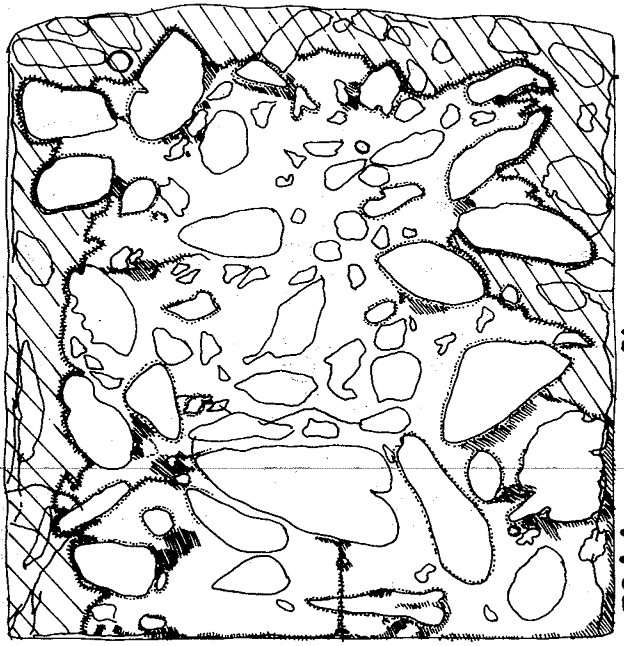
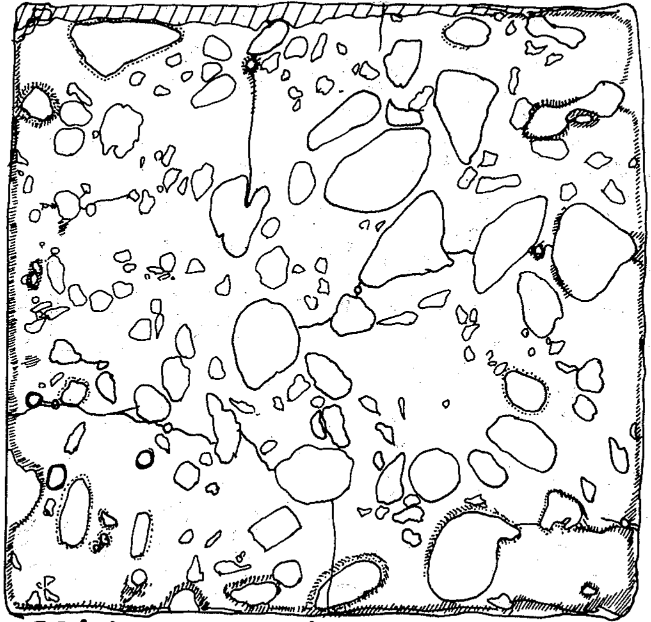
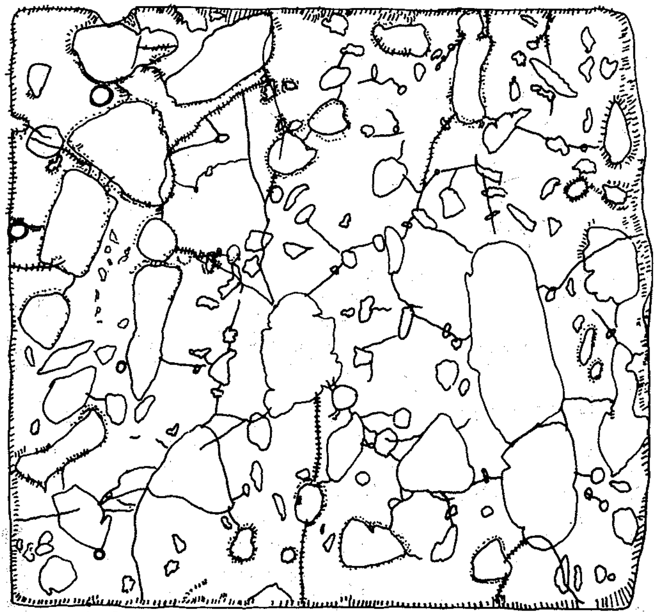


Fig. 4 F8/I/3

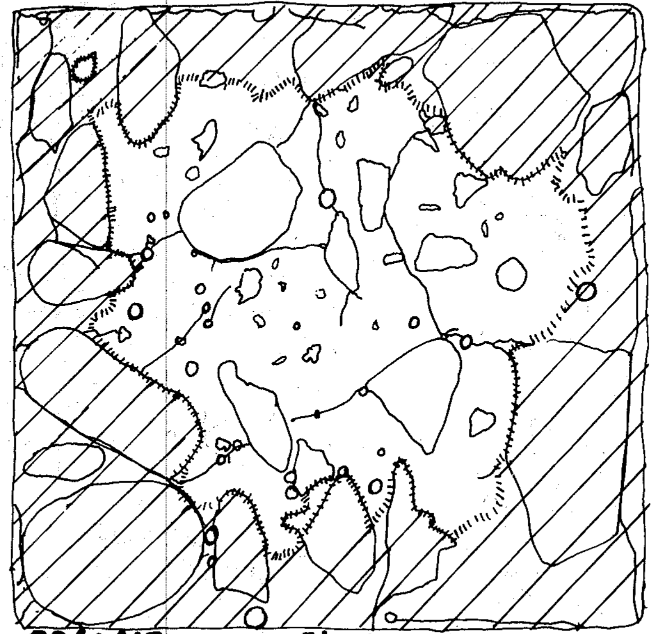
F8/1/6 Fig. 4



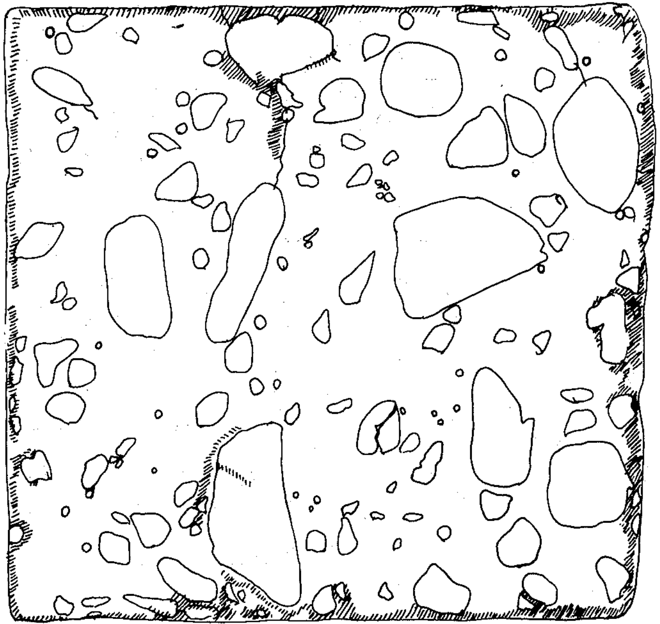
F8/1/5 Fig. 4



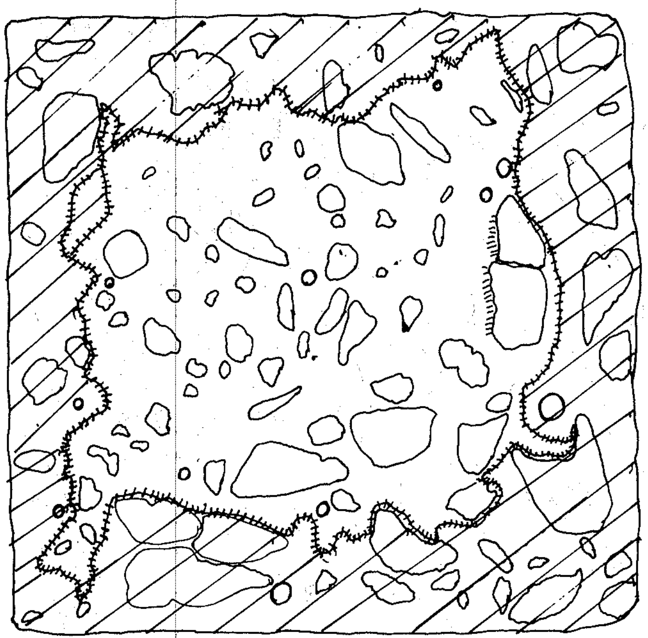
F8/1/7 Fig. 4



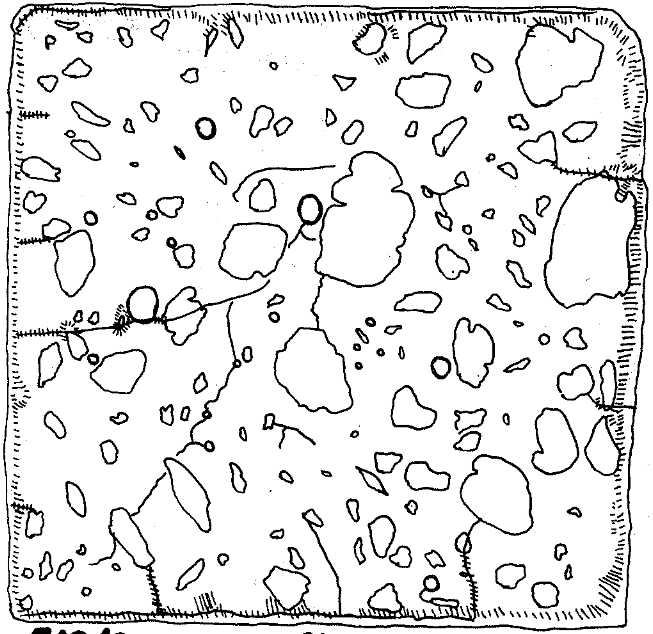
F8/1/12 Fig. 5



F8/1/13 Fig. 5



F10/4 Fig. 6



F10/9 Fig.6

ION-EXCHANGEABLE SODIUM IN CONCRETE AGGREGATES

Clifford White

Blue Circle Southern Cement Ltd

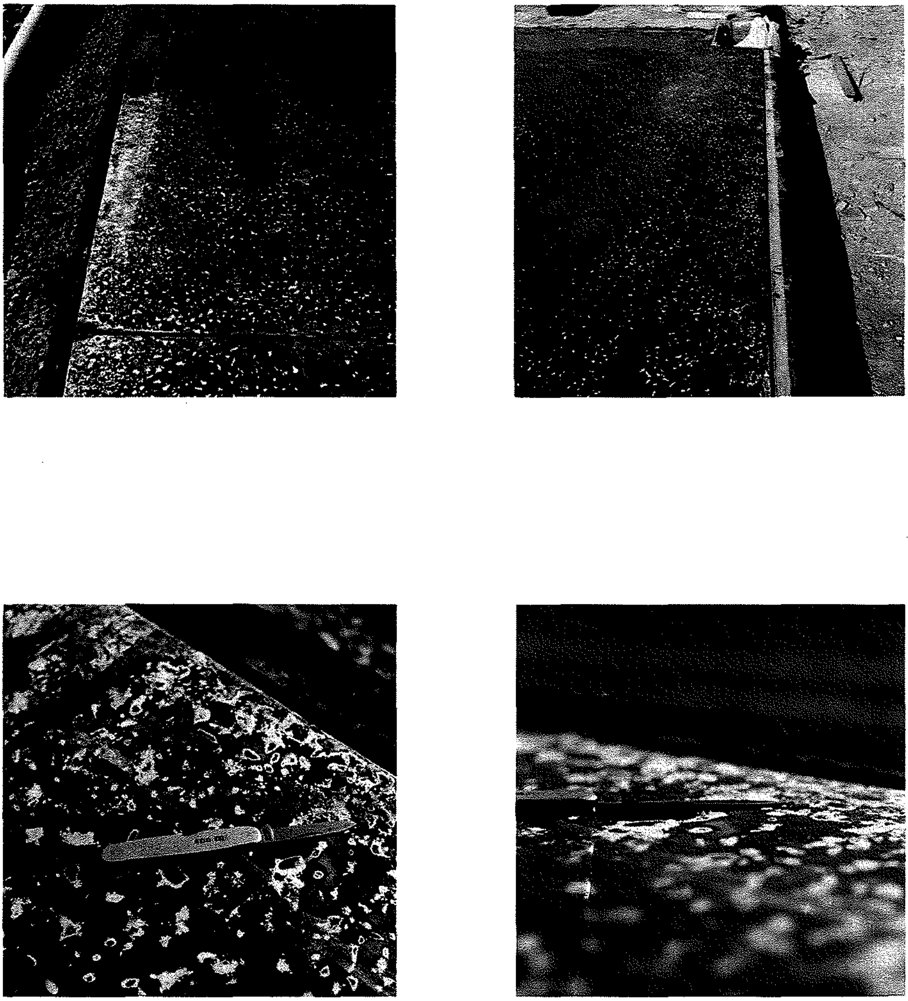
This phenomenon was evidenced due to the coincidence of very unusual weather conditions and concreting techniques.

A call was received from a major concrete customer at approximately 2:30 in the afternoon, describing that the slab which he had poured some two hours previously, was now covered in white snowflakes. The temperature was 43°C, the relative humidity approximately 25% with a 15 knot wind and the major part of the eucalypt forest 25 miles to the windward of the area was on fire. After suggestions that the snowflakes were woodash were badly received, a trip was made to the site and the attached photographs were taken.

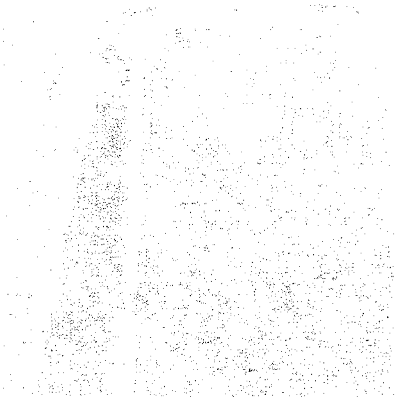
The photographs show that very large areas of the slab, which had just passed the stage of final set by Proctor Penetrometer, were covered in white growths of very fine pure white micro-crystalline material, in many cases standing up above the slab by up to 3 and occasionally 4 mm. Most of these white deposits were in the form of rings clearly outlining aggregate particles presumed to be in the proximity of the surface of the slab. The phenomenon was intriguing and careful sampling of the white material was carried out and proved to be rather difficult as it was very similar to attempting to sample snowflakes but probably of an even lower bulk density. Areas of the slab which had been poured later and which had not "fully set", were still showing growth of the white material. A rapid attempt at analysis of the white powder indicated some 23% Sodium Oxide (Na_2O), together with less than 1% of Calcium Oxide (CaO), and about 7% of Sulphur Trioxide (SO_3). The rest of the material was organic producing a strong odour of burning wood on charring and ignition. Initial reaction was that a mis-delivery had been made of Sodium Ligninsulphonate instead of Calcium Ligninsulphonate, but this evinced a strong denial by the suppliers and quick evidence that the assumption was incorrect. Certainly the white crystalline powder contained the sodium salts of ligninsulphonate and probably some other sodium organic compound, and the trace of calcium was probably due to sampling contamination. The distribution of the white rings immediately suggested that bleed water, initially retained beneath pieces of aggregate, was seeping up to the surface especially around the edges of the aggregate, carrying with it the white soluble material which was then deposited by evaporation on the surface due to extreme temperature and humidity conditions.

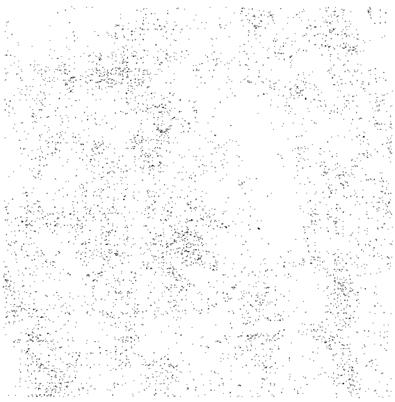
The cement which had been used was well-known to be very low in sodium oxide and the source of the apparent large quantity of sodium was a puzzle although it will be appreciated that a mass balance was not possible.

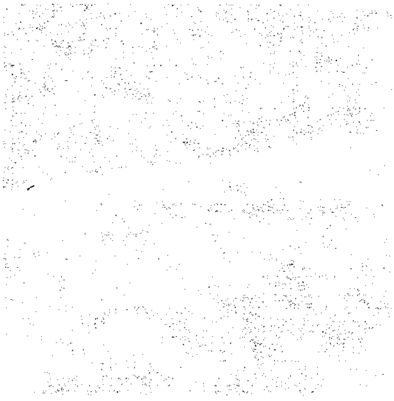
The aggregate used was one very commonly used in the Sydney area at that time, being classified as a basalt with some parts more or less vesicular. On enquiry, it was discovered that the quarry was a well-known source of large botryoidal masses of prehnite but there was no evidence in any of the aggregate in the supplier's bins of any such material. Tests on the aggregate which were made by suspending it in, first, cement suspensions and later, in order to avoid "blanks", in hydrated lime suspensions, quickly showed that considerable amounts of sodium oxide were liberated into solution, in the extreme representing 3 and 4 times the amounts which would have been liberated in the same time by a cement suspension of concentration equivalent to that in a typical concrete. It was then assumed that the phenomenon was due to such ion-exchange reaction from other zeolites occurring, followed by crystallization of the least soluble sodium salts accumulating in the rising bleed water. Tests on several other commercially available basalt aggregates in Australia have shown similar potential for ion-exchange reactions to occur whilst a fluid phase exists capable of ion migration.

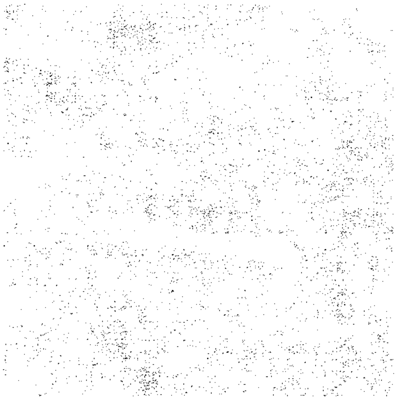


Photographs illustrating the white micro-crystalline growths









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VAL DE LA MARE DAM
JERSEY, CHANNEL ISLANDS

Lewis H. Coombes
Engineering and Resources Consultants

ABSTRACT

Val de la Mare Dam is the principle storage reservoir for the Island of Jersey. The dam has been regularly inspected since completion in 1962.

In January, 1971, small upstream relative movements of the handrail of the crest walkway bridge were noticed. At the same time, darkening and damp patches were observed on the downstream face of the dam and parts of the surface showed random cracking of the concrete.

Ercon were retained to investigate the problem, and a programme of investigations was initiated. Alkali aggregate reactivity was diagnosed as the cause of the defects.

Proposals were developed, and subsequently implemented, for remedial works which included the provision of drainage into the gallery, the grouting of and the installation of anchors in a section of the dam most adversely affected by the reaction, and the installation of appropriate instrumentation to monitor the loads on the anchors, future movements of the particular section, and uplift pressures.

Introduction

The dam has a maximum height of 23 m above the valley floor, a crest length of 170 m, and is constructed of mass concrete in 6.7 m wide blocks with the lift (pour) heights being generally 1.2 m. The foundation is of Precambrian sedimentary shales.

The dam was designed using the middle third rule allowing for an internal uplift pressure of 50% of reservoir head at the upstream face decreasing linearly to zero at the downstream face, based on 100% of plan area.

Construction took place over the period 1957 to 1962, with the coarse aggregate being obtained from a local quarry, and from oversize material from a beach, the fine aggregate from a beach, and the cement being imported from the U.K. A photograph of the dam is shown in Fig. '1'.

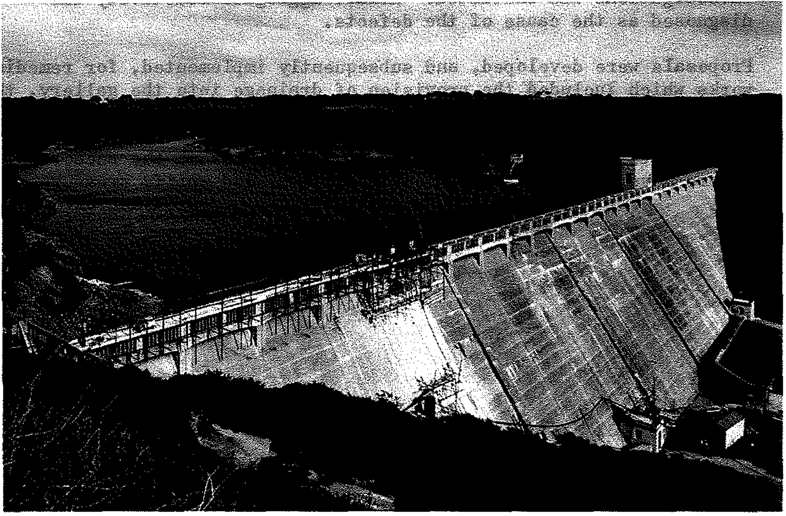


FIG. 1
Val de la Mare Dam

The first signs of trouble appeared in January 1971, following a period of colder than usual weather. Small upstream relative movements in the order of 6 to 12 mm were noticed on certain sections of the concrete handrail of the crest walkway bridge, and darkening and damp patches were observed at the same time on the downstream face of the dam on the same blocks on which the movements had occurred, with the surface showing random hairline cracking.

Following Ercon's initial inspections of the dam and the quarry, it was thought likely that alkali aggregate reaction could be the cause of the problem even though the aggregate quarry had been in operation for several years and there had been no published records of an occurrence on Jersey. A programme of investigations was therefore initiated. Also several theories, including frost action, sulphate attack and earthquake action, were considered and investigated, but eventually discounted.

Investigation Programme

The investigation programme, which was carried out during the period July 1971 to September 1973, included the following :-

(i) Consultations with the Cement and Concrete Association, the American Corps of Engineers, the Concrete Research Laboratory in Karlstrup, and the British Museum (Natural History), Department of Mineralogy. The consultations were linked with a review of the existing literature on the subject which revealed that experience of the phenomenon in the U.K. was limited. Overseas case histories were therefore examined and discussed, and visits were paid to Jersey by specialists in the field of testing and deterioration of concrete.

(ii) Review of the method and sequence of construction of the dam and of the source of supply of the relevant construction materials :- investigations revealed that affected lifts were randomly sited in the dam, but were associated in time.

(iii) Discussions with the U.K. Suppliers on the cement shipped to Jersey during the appropriate period of construction. These discussions revealed that cement shipments to Jersey in 1960 during periods significantly related to the time of construction of affected block lifts contained cement with alkali contents of values up to 0.95 percent measured on a monthly average basis and expressed as a percentage of Na_2O.

(iv) Geological survey of, and testing programme on aggregate samples from, the local quarry, and examination of the sources and testing of samples of the local beach sand. Reactive materials were identified in some of the materials obtained both from the local quarry and from the beach, and a materials testing programme was initiated.

(v) Core drilling in specific sections of the dam, followed by laboratory description and testing.

(vi) Petrographic examinations of thin sections of the concrete cores and of the aggregates from sources considered to be the same as used in the concrete and from various other localitities on the island - carried out by Ercon and by the Building Research Establishment. The examinations showed that the samples contained reactive silica which could give rise to alkali aggregate expansive reactions. The silica was present as either opal or chalcedony.

(vii) Expansion testing on cores taken from the dam and on mortar bars made from local quarry rock and beach sand - carried out by the Building Research Establishment. The mortar bar tests on the aggregate samples showed that the aggregates were expansive.

(viii) In-situ sonic velocity measurements in each accessible lift of each block of the dam. A first series of measurements was carried out in September 1972, and a second series in July 1973. The technique was used largely to give a qualitative assessment of the concrete quality, and four classifications of concrete were made on the basis of the measured velocities. Comparisons were made between the two series of measurements, and areas of significant deterioration were identified by significantly lower velocities.

(ix) Installation of electrically operated piezometers in certain sections of the dam, the locations chosen on the basis of the sonic test results. The limited number of piezometers installed indicated that the original design uplift pressures were not being exceeded, except in the case of Block 6 where the higher pressures were resulting in a reduction in the design factors of safety against overturning and sliding.

Assessment of Remedial Measures

Following the investigation programme and instrument readings taken over a period of more than two years, the decisions then had to be made on:-

(a) Whether or not the dam would eventually deteriorate to the point of being unserviceable.

(b) If so, how long could it remain in service before an alternative water supply source had to be found.

(c) If not, what remedial works were required to keep the dam in a safe stability condition.

It was not possible to make a completely quantitative decision on the matter. Engineering judgement, based on the whole range of accumulated information, and taking into account social and economic factors, had to enter into the decision.

Several general factors were of significance and influenced the ultimate decision :-

(i) Although the reactive material had to be assumed to be present throughout the dam, the degree of attack and concrete deterioration varied. This was borne out by the sonic test results, the crest movements and visual inspection of the downstream face of the dam. The known variation of alkali content of the cement delivered and the fact that most of the reactive material was thought to be derived from a number of veins in the quarry and from beach pebbles, containing either chalcedony or opal, also supported this assessment.

(ii) The expansion test results carried out by the Building Research Establishment on concrete cores from the dam containing suspected reactive material and on mortar bars manufactured from coarse aggregate from the Ronez Quarry and beach pebbles, all containing reactive silica, indicated that the degree of expansion was not as high as the values considered unacceptable in the U.S.A. and Canada, based on A.S.T.M. C. 33-67 and C.227-69.

(iii) Case studies of other dams indicated that the initial large rate of expansion caused by the reaction was not maintained with time.

(iv) There was no proven method of chemical treatment that would either stop or reduce the reaction and expansion.

(v) The readings of internal uplift pressures from the installed piezometers were acceptable, except in the case of Block 6.

Based on the evidence accumulated on this particular dam and on the results of other cases, a conclusion was reached that the concrete would not deteriorate to the extent that it would be incapable of taking the required compressive loads. The danger was that expansive cracking could lead to higher internal uplift pressures than had been allowed for in the design, resulting in instability.

Hence, the policy was adopted of proceeding with remedial works to ensure that the stability of the dam was maintained against increased internal uplift, assuming that the concrete would be capable of taking all the stresses applied to it in the future. Also, as the alkali aggregate reaction varied over the dam, only isolated bad sections would be dealt with, and the remedial method adopted should be capable of being extended in stages to the complete dam at a later date should further deterioration occur. Any remedial works adopted had to be such that the reservoir could be kept in operation at all times, and a minimum of restriction placed on the water level during the work.

Decision on Remedial Measures

After consideration of many alternatives, the decision on the type and extent of remedial measures was made related to Block 6 and Blocks 10-20. Block 6 is situated near the right abutment, and is clearly indicated on Fig. 1 by the presence of scaffolding and equipment. Blocks 10-20 are in the centre section of the dam between the two gallery openings sited against the downstream toe.

Block 6

The remedial measures chosen for Block 6 had two main aims. Firstly, grouting was proposed as a trial measure to ascertain whether a curtain could be introduced near the upstream face of the block to reduce seepage uplift pressures and to reduce future alkali aggregate reaction by limiting available water. Piezometers could also be installed to check the effects of the curtain.

Secondly, to counteract the higher internal uplift pressures, it was proposed to anchor the block to the foundation rock beneath the dam by installing prestressing tendons. The required anchor force would be determined from static considerations of stability to provide for a minimum factor of safety against overturning of 1.7 under full flood condition loading and with hydrostatic uplift assumed to act over 100% of the plan area of the block, with full hydrostatic head at the upstream face decreasing linearly to zero at the downstream face.

Blocks 10-20

On the remainder of the dam, it was not considered essential to undertake any remedial works. However, since drilling equipment would be mobilised, for Block 6 work, it was decided to take advantage of this by drilling drainage holes approximately 1.2 m from the upstream face of the dam in Blocks 10-20 where access was available from the inspection gallery. It was hoped that if cracking became serious, the holes would intercept seepage flow and reduce the internal uplift pressure downstream of the holes.

Remedial Works

The remedial works were carried out during the period June to December, 1974.

Site Investigation

As a necessary preliminary to the design of the anchoring of Block 6, an investigation of the foundation rock beneath the block was carried out. Two vertical boreholes and one inclined borehole were drilled from the downstream toe of the block. The inclined borehole was angled to penetrate through the middle of the proposed anchorage zone.

In addition, one vertical borehole was drilled from the crest of Block 6, down through the concrete of the dam into the proposed anchorage zone. The position in plan of this hole coincided with one of the proposed grout holes in the centre of the block (refer to Fig. 2). Laboratory tests were carried out on cores recovered from the boreholes - the tests produced data on the elastic modulus and poissons ratio of the rock, and the shear strength of the joints. All boreholes encountered very jointed and fissured rock.

In addition to the boring, rock outcrops in the vicinity of the dam were mapped geologically to supplement the borehole information.

Grouting of Block 6

Six holes were drilled vertically down through the concrete of the dam at a distance of 1.2 m from the upstream face and between 0.9 m and 1.32 m apart. Five of the holes were drilled in 80 mm diameter - the depth of the holes varied from 13.5 m to 17.0 m such that the bottoms of the holes were approximately 0.6 m into the concrete of the cut-off trench. The sixth hole, chosen as the position of the site investigation borehole, was cored in 100 mm through the concrete and foundation rock for a total depth of 34.5 m The positions of the grout holes are shown on Figs. 2 and 3.

A water test was carried out in each hole to test the permeability of the surrounding concrete - the tests showed the permeability to be very low.

The material chosen for grouting was Polythixon 60/40 DR grout. This is an oil-based chemical grout supplied in the form of two liquid phases which, when mixed, form a cross-linked polymer that sets to form a rubber-like substance. At the time of mixing, the grout has a very low viscosity and is therefore suitable for penetrating fine cracks. The quantity of Polythixon used in the grout holes was only slightly greater than the quantity of water used in the water tests, so it is probable that very little penetration was achieved.

Anchoring of Block 6

In order effectively to distribute the loads from the anchors, a high-strength reinforced concrete spreader beam was introduced as part of the crest lift of the downstream face extending for the full block width between the walk-way supports. The spreader beam was installed before any drilling work was carried out for the grouting, anchor tendons and instrumentation, and to avoid drilling through the freshly placed concrete of the spreader beam for the grout holes and the tendon holes, mild steel tubes were fixed in appropriate positions through the beam.

The anchoring of Block 6 consists of 3 No. 40 mm diameter 'Macalloy' high tensile anchors fixed in 115 mm diameter holes positioned symmetrically across the width of the Block at 2.23 m centres and drilled through the concrete of the dam into the foundation rock - refer to Figs. 2 and 3.

Calculations for the proposed depths and lengths of the anchorage zones were carried out using data from the laboratory testing of rock cores. Using the depths and anchorage lengths resulting from the analysis, a computer analysis of stresses and displacements in the dam and the foundation was carried out using a finite element technique based on the linear elastic plane strain model. The results of the computer analysis showed that there would be no areas of high stress concentration after the installation of the anchors and no excessive movements of the structure.

The final depths at which the anchorage zones were established were in fact much deeper due to the rock conditions encountered during drilling for the anchors. A major shear zone was detected below Block 6, lying parallel to the bedding and therefore dipping steeply upstream and towards the centre of the valley. Numerous fissures and areas of highly fractured brecciated rock associated with this shear zone were observed.

No problems were encountered drilling through the concrete of the dam - drilling was carried out using a 115 mm diameter down-the-hole hammer.

Drilling through rock was good initially until the highly fractured zones were encountered - in these zones the drill repeatedly jammed. When the hammer was freed and operating again, gravel size fragments of mudstone and some clay were flushed up the borehole. Collapsing of the holes frequently occurred, giving concern over the possibility of cavities being created in the fault zone.

In order to prevent further collapse in the holes and the formation of cavities, the method of drilling was changed from rotary percussive to coring using water flush, and a drilling/pressure grouting technique was employed. Repeated pressure grouting and re-drilling resulted in a build-up of grout in the fault zone, and the area was eventually stabilised. One of the advantages of the change in drilling method was that the rock cores could be examined and a better appreciation of the geology of the zone could be obtained.

Although the cores showed the rock in the chosen anchorage zones to be suitable, fissures and joints were noted in these cores, and water tests showed a sufficiently large take from the anchor holes for fissure grouting to be considered necessary.

Grouting was carried out in stages up each hole using hydraulic packers - the quantities of grout pumped were not high indicating that no large voids were present. When set, the grout was redrilled and the grouting repeated until water tests showed the anchorage zones to be tight.

As the anchors were being installed, denso tape was wrapped around the bars for approximately 3.0 m above the bonded zone and above this silicon grease was sprayed onto the bars. The presence of the denso tape immediately above the bonded zone ensured that there would be no transfer of bond stress between the anchor tendon and the rock at a higher level than was desirable.

The anchors were bonded to the rock over a 9.75 m anchorage length using a 0.45 w/c low alkali cement grout with a 14-day cube strength of 35N/mm^2. The grout was pumped through a 12 mm diameter pipe that was temporarily fixed to the lower end of the anchor sleeve and raised as grouting proceeded.

As a test of the ability of the foundation rock to carry successfully the anchor loads at the chosen depths, the centre anchor was stressed before drilling of the two outer anchors had been completed.

Stressing on all three anchors took place in 10-tonne increments up to 90 tonnes with readings being taken of the anchor bar extension, the load cells, the electrolevel and the inverted pendulum after each increment. Readings were plotted so that anything unusual would have been detected. After a waiting period of approximately 15 minutes, the load was increased by a further increment. At 90 tonnes, the load was held for 30 minutes before being relaxed to the design figure of 85 tonnes, and locked off. Readings of the demec points and the two extensometers were taken before and after each stressing operation.

When the two anchors had been stressed, the annular space above the bonded length of each anchor tendon was filled with Polythixon FR special grout to prevent corrosion of the tendons.

Instrumentation Installation

Instruments were installed in and adjacent to Block 6 to monitor behaviour during the stressing of the anchors and at regular intervals after the stressing. The individual sitings of the instrumentation are indicated diagrammatically on Figs. 2 and 3.

In Block 6 itself, the following instruments were installed :-

(i) Vibrating wire load cells at the head of each anchor.

(ii) A vertical extensometer down from the walkway bridge to a level five feet below the deepest anchor.

(iii) An inclined extensometer from a point two-thirds down the exposed downstream face of the dam through the cut-off trench into the foundation zone immediately upstream of the dam.

(iv) An inverted pendulum vertically down from the walkway bridge to the middle of Lift No. 7.

(v) Two electrically operated piezometers inclined down from the downstream face of the dam into the middle of Lift No. 5, the individual piezometers being positioned 1.5 m and 3.35 m from the upstream face of the dam.

(vi) Twenty four mechanical strain gauge positions (three points per position) on the downstream face of the dam distributed across the lift joints and the vertical joints at each side of the block.

In addition to the above, four electrolevels were positioned on the walkway piers, each electrolevel spanning the joint between adjacent blocks for Block Nos. 4 to 8.

Relief Drainage Holes in Blocks 10 - 20

The relief drainage works consist of 75 mm diameter holes drilled from the roof of the drainage gallery up to near the crest of the dam, and from the bottom of the gallery down to elevation 3.35 m as shown on Fig. 4.

The upward holes are vertical, with respect to the dam elevation, in Blocks 10 to 18, and were drilled generally at 3.35 m centres, except in three blocks where the regular spacing was adjusted to avoid clashing with existing piezometer installations. Inclined holes, with respect to the dam elevation, were provided for Blocks 19 and 20. The downward holes are vertical with respect to the dam elevation, and are again generally at 3.35 m centres, and were extended into the foundation rock to supplement the existing foundation relief drainage system.

The upward holes were capped at their exit points near the crest to prevent the ingress of water and dirt - the caps are removable for inspection and maintenance purposes. Both the upward and downward holes were provided with suitable capped ends in the gallery to facilitate measurement of flow.

Future Monitoring

Surveillance of the dam is continuing, principally by continual visual observation of the downstream face and of any movement at the crest of the dam, supported by readings on the piezometers and other instruments in Block 6 and by records of the flow from the drainage holes in Blocks 10 - 20. Sonic testing is also planned at three-year intervals.

Acknowledgements

The Author is grateful to the Directors of the Jersey New Waterworks Company for permission to present this paper.
This paper contains extracts from a Paper presented at the BNCOLD/University of Newcastle Symposium on Inspection, Operation and Improvement of Existing Dams held at the University of Newcastle upon Tyne in September, 1974.

Reference

L.H. COOMBES, R.G. COLE and R.M. CLARKE

Remedial Measures to Val de la Mare Dam,
Jersey, Channel Islands, following
Alkali Aggregate Reactivity.
BNCOLD/University of Newcastle upon Tyne
Symposium, 1975.

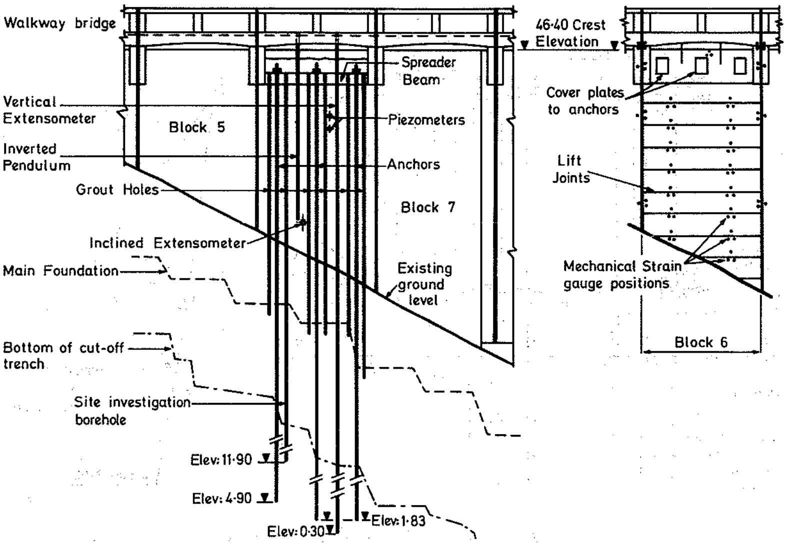


Fig.2 Locations of anchors, grout holes and instrumentation in Block 6.

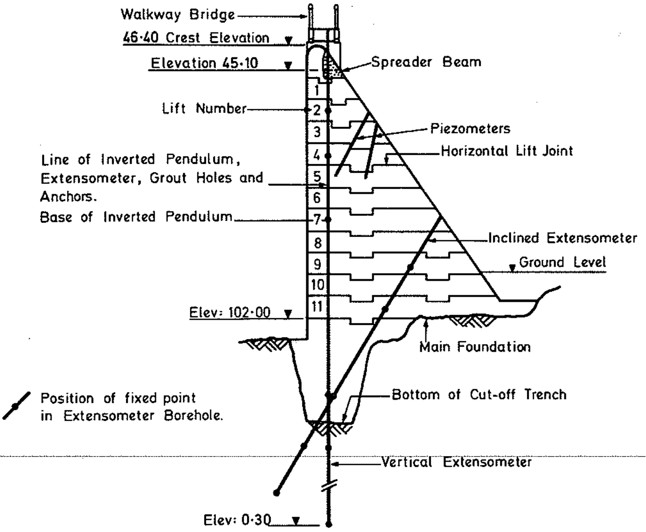


Fig.3 Section through Block 6 showing arrangement of anchors, grout holes and instrumentation.

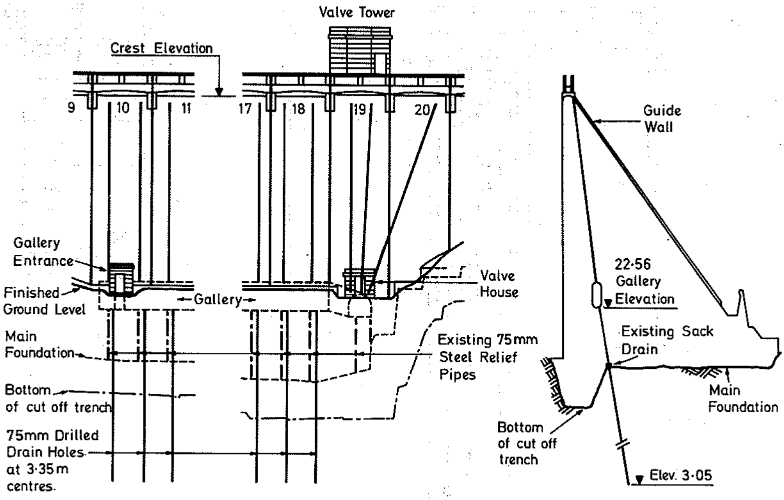


Fig.4 Relief Drainage Holes.

PROFESSOR DIAMOND'S SUMMARY OF PROCEEDINGS

A REPORT

Professor Diamond expressed the view that although some of the papers presented at this Symposium deviated from the strict subject title of the meeting, a wealth of new technical information had been presented which indicated healthy and flourishing research in this field of study.

The papers could perhaps be grouped into the following general areas of study: the effects of alkalies on concretes, the effects of alkalies in cements, the study of the potential reactivity of aggregates, consideration of the detailed reaction mechanisms, consideration of the effects of pozzolans on reactivity, field reports and case study investigations, reports of remedial work and reviews of the subject such as that presented by Vivian.

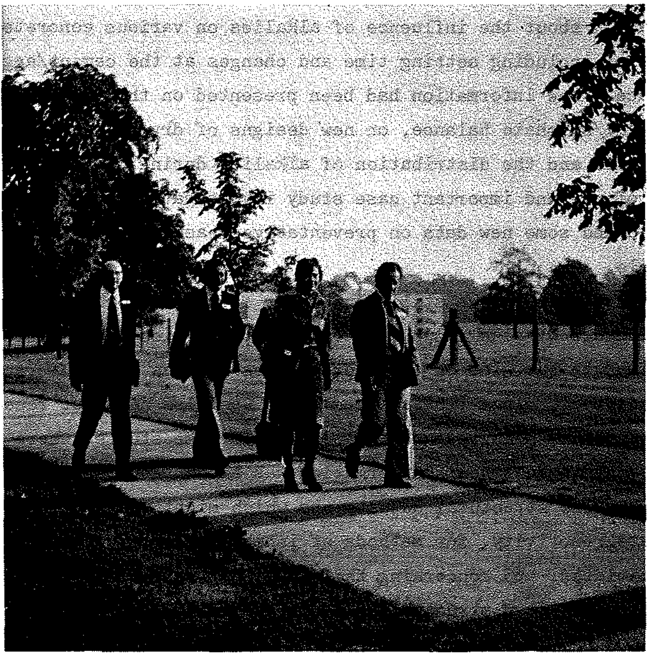
Delegates attending this Symposium had received much new information about the influence of alkalies on various concrete properties including setting time and changes at the cement/aggregate interface. New information had been presented on the importance of the alkali/sulphate balance, on new designs of dry process cement manufacture and the distribution of alkalies during manufacture. A number of new and important case study investigations have also been reported and some new data on preventative measures has become available.

However, there was still a need for further information concerning the influence of alkalies on the various properties of concrete,not just strength but also on other properties such as set, interaction with additives, glass fibres etc. There was also need for research on preventative measures and for reports of case studies where remedial measures had been taken. Information was also urgently needed concerning the structural adjustments which might result from alkali-aggregate reactivity, for methods of inhibiting or slowing reactions once initiated, and concerning the cosmetic treatments which might be applied to affected structures.

CONTRIBUTION TO DISCUSSION

Mr. K. Brittain

May I please make one comment concerning Dr. Diamond's excellent review of the proceedings of this symposium and the tasks to be dealt with, I suggest that as well as case studies, we must have an assessment of the frequency of damage, either structural or superficial to buildings in each area. If national guidance is to be given, the scale and emphasis must relate to the anticipated need.



Delegates at C. & C. A.

LIST OF DELEGATES

Dr Johan Alexanderson	Siporex A B, Sweden
Dr Sahil Alsinawi	University of Baghdad, Iraq
Dr Haraldur Asgeirsson	Building Research Institute, Iceland
Mr Anthony Baker	Queen Mary College, U K
Dr Robert Bakker	Concrete Research Institute, Holland
Dr Donald Barlow	Rugby Portland Cement Company, U K
Mr Kenneth Brittain	Association Portland Cement Manufacturers Limited, U K
Mr Lewis Coombes	Engineering & Resource Consultants Ltd, U K
Dr Jurgen Dahms	Cement Industry Research Institute, W Germany
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Mr John Flanagan	Portland Cement Institute, South Africa
Dr Peter Fookes	Consultant, U K
Dr William French	Queen Mary College, U K
Dr Patrick Grattan-Bellew	National Research Council, Canada
Dr Gudmundur Gudmundsson	State Cement Company, Iceland
Dr Dieter Hirche	Federal Water Authority of Bavaria, W Germany
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