THE CONTROL OF ALKALI SILICA REACTION USING BLENDED CEMENTS.

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SUMMARY

It has been previously established that alkali silica reaction (ASR) in concrete may be controlled by blending Portland cement with suitable hydraulic or pozzolanic materials. The controlling mechanism has been attributed to the dilution of the cement's alkali content and reduced mobility of ions in concrete's pore solution. In this project an attempt has been made to identify the factors which influence the relative importance of each mechanism in the overall suppression of the reaction by the use of blended cements.

The relationship between the pore solution alkalinity and ASR was explored by the use of expansive mortar bars submerged in alkaline solutions of varying concentration. This technique enabled the blended cement's control over expansion to be assessed at given "pore solution" alkali concentrations. It was established that the cement blend, the concentration and quantity of alkali present in the pore solution were the factors which determined the rate and extent of ASR.

The release of alkalis into solution by Portland cements of various alkali content was studied by analysis of pore solution samples expressed from mature specimens. The specification for avoiding ASR by alkali limitation, both by alkali content of cement and the total quantity of alkali were considered.

The effect on the pore solution alkalinity when a range of Portland cements were blended with various replacement materials was measured. It was found that the relationship between the type of replacement material, its alkali content and that of the cement were the factors which primarily determined the extent of the pore solution alkali dilution effect.

It was confirmed that salts of alkali metals of the kinds found as common concrete contaminants were able to increase the pore solution hydroxyl ion concentration significantly. The increase was limited by the finite anion complexing ability of the cement.

KEY WORDS. Blended cements, alkali silica reaction.
Pfa, slag, alkalis.

This work is dedicated to the memory of Rosemary Canham and Louise Shea.

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LIST OF CONTENTS

List of Tables

CHAPTER 3. **PAGE**

APPENDIX 2

APPENDIX 3 PAGE

APPENDIX 4

APPENDIX 5

APPENDIX 6

APPENDIX 7

List of Figures

CHAPTER 1 PAGE

CHAPTER 2

CHAPTER 3

CHAPTER 6

APPENDIX 1

APPENDIX 3

PAGE

APPENDIX 4

APPENDIX 5

PAGE

APPENDIX 6

PAGE

APPENDIX 7

GLOSSARY OF ABBREVIATIONS

AAR	Alkali aggregate reaction
ASR	Alkali silica reaction
Ash	Pulverized fuel ash
pfa	
Slag	Ground blastfurnace slag
gbfs	
$Na_2O\%$	Equivalent soda content to B.S 4550 part 2: 1970
C_3S	Tricalcium silicate $3CaO\ SiO_2$
C_2S	Dicalcium silicate $2CaO\ SiO_2$
C_3A	Tricalcium aluminate $3CaOAl_2O_3$
C_4AF	Tetracalcium aluminoferrite $4CaO\ Al_2O_3\ Fe_2\ O_3$
MIP	Mercury intrusion porosimetry
To	Time to initial expansion (hours)
HA, F	High alkali content, fine pfa
HA, C	High alkali content, coarse pfa
LA, F	Low alkali content, fine pfa
LA, C	Low alkali content, coarse pfa
CORR°. CONC	Corrected ionic concentration
QTY	Quantity
SOLN	Solution
g	gramme
PROP	Proportion
CC	Cement content (Kg/m^3)
AC	Aggregate cement ratio

CHAPTER ONE INTRODUCTION

1.1 Statement of the Problem

Alkali aggregate reaction (AAR) is the collective term for deleterious interactions between certain aggregates and the alkaline pore fluids of concrete. The expansive reactions involved may be of several forms known as alkali carbonate reaction, alkali silicate reaction and alkali silica reaction. The alkali silica reaction (ASR) is relatively common throughout the world and, to date, is the only form of AAR reported to have occured in the United Kingdom. The other two forms of the reaction are comparatively rare and confined only to certain countries.

Compared to the volume of concrete produced by the construction industry, the extent of the ASR problem is limited. However, concern is expressed over the ever increasing number of instances of ASR being recorded in the United Kingdom. The frequency of aggregate related durability problems in concrete is expected to increase in the near future as a result of the present trends in concrete manufacture and usage. Attempts by the industry to comply with environmental protection legislation and to reduce the costs of production have resulted in cements of increased alkali content(1). This together with the use of poorer quality aggregates combined with the current requirement for strong, cement rich concretes are also causes for concern.

1.2 Historical Background

ASR was first recognised in America during the mid 1930's when a number of relatively new concrete structures developed random cracking, from which a gel was observed to be exuded. T E Stanton(2) determined that this cracking was due to an expansive gel formed by a reaction between siliceous aggregates and cements with high alkali metal contents.

During the 1940's and 1950's, the ASR was investigated further. American research was directed at the actual mechanism of the reaction and secondly at the mechanisms by which the reaction could be controlled. The mechanism of reaction was established but the method by which the gel imbibed water so causing the damaging expansion produced many conflicting hypotheses. Hansen(3), suggested that the expansive gel worked as an osmotic cell and this idea was supported by some workers(4,5). However, other workers(6,7,8) concluded that the cracking was due to mechanical pressure generated by the gel product in its solid or quasi-solid state. Research into the control of expansion was initiated by Stanton(9), who had observed that certain siliceous admixtures could prevent or reduce reactive expansion. Further investigation proved that many pozzolanas when blended with Portland cement had the ability to control the reaction(10,11). In 1951, Barona de la 'O Fedrico demonstrated that ground blastfurnace slag had a similar effectiveness and this was later verified by other workers(12,13).

The volume of research work into alkali aggregate reaction was considerably reduced by the end of the 1950's. Some research was continued by countries where ASR represented a serious threat (due to national geographical resources) noteably Denmark and Iceland. Interest in ASR was rekindled in the mid 1970's, particularly in America, Canada, Great Britain, India, Japan and New Zealand(14), where occurences of ASR were diagnosed. The interest in the ASR has been maintained to date. Research and discussion of experience of the subject has been exchanged at seven international symposia. The preface to the proceedings of the last symposium in 1986 reported that over 100 papers from 21 countries were received, reflecting the current interest in the subject. The main research interests during this period were the use of blended cements, their hydration and the mechanisms by which the replacement materials control expansion due to ASR. (20-22). A considerable quantity of work on the assesment of various pozzolanic and hydraulic materials and their effectiveness in reducing ASR expansion has been carried out, using a variety of techniques. Many workers(16-18) have used expansive mortar bars to assess the relative performance, while others, notably Diamond(23) have expressed and analysed the pore solution of blended cements. Their findings have indicated that an important relationship exists between the alkali content of cements and the ASR. However, there has been much debate on the use of high alkali replacement materials, as the role and availability of the alkalis contained in the replacement materials is not fully understood. A number of workers(23,38,39) using ashes and slags of various alkalinities blended with various cements have reported that the replacement materials may control ASR by diluting the cement alkalis.

Nixon and Gaze(40), however, reported that experiments monitoring length change of mortar bars indicated that the reduction in expansion achieved by the addition of pfa's was greater than that which have been achieved solely by alkali dilution. Other workers((20,21,42,43) have noted that the blended cements produced a much denser microstructure than comparable plain cements. This increased fineness in microstructure has also been put forward as another possible mechanism for the control of ASR expansion. Bakker(22), Regourd(42) and Sersale and Frigione(43) also observed that slag blended cements had denser compact calcium silicate hydrate (CSH) gel containing little or no calcium hydroxide. This is thought to reduce the mobility of the alkali ions from the pore solution in the transportation of the ions to the silica reaction sites, and the permeability to water.

Therefore, it is currently suggested that when pozzolanic or hydraulic materials are used to replace a proportion of Portland cement, there are probably two separate mechanisms which control the expansion due to ASR. These are the dilution of the cement's alkalis and/or increased fineness of the cements' microstructure.

1.2.1 Historical Review of ASR in Great Britain

The first work published in connection with ASR in Great Britain dates back to the late 1940's. The work reported the findings of examinations carried out on an extensive range of aggregate sources in the United Kingdom(44). Although the use of siliceous aggregates is widespread in the U.K it was concluded in this work that not one of the aggregates tested was reactive and therefore ASR was thought unlikely to be a problem in Britain.

The first recorded occurence of ASR was reported in 1971, when the Val-de-la-Mare dam in Jersey was found to exhibit cracking. By 1976 several structures in the south west of England were diagnosed as suffering from ASR. At this time all the mainland occurences had been attributed to marine-dredged aggregates. By the late 1970's several cases documenting land-won aggregates had been recorded(45). The number of occurences has continued to increase, although they appear to be mainly confined to specific geolographical areas in the south west of England and the Trent valley as shown in figure 1.1. The larger affected structures which required expensive repair, for example, the Royal Devon and Exeter hospital and the 350 midland link motorway bridges which were suspected to be suffering from ASR attracted widespread attention from both British trade journals(46,47) and the national press(48,49). To date, only

Figure 1.1

Location of reported cases of ASR in the United Kingdom as recorded in 1983

(Reproduced from ref 51. by kind permission of Mr D. Palmer) one affected structure, a bridge, has had to be demolished before completion of its expected service life(50).

The British cement and concrete industry recognized ASR as being a potentially very serious problem, a problem which many design engineers, material suppliers and contractors within the industry knew very little, if anything about. In the early 1980's, an independant working party, consisting of specialists from all areas of the concrete and aggregate industries was set up to provide advice for the industry on ASR. The findings of the working party were published by the Cement and Concrete Association in September 1983(51) and revised in 1985. The findings were presented in the form of guidance notes for engineers and contractors on how to minimize the risk of ASR occuring in new structures. The report represents the combined experience of the industry and reflects the present state of knowledge on this subject. It provides the most comprehensive practical guide on the methods to minimize the risk of ASR available at this time.

1.3 The ASR Mechanism

ASR is a long term phenomomen which may take 5 years or longer to become evident. Often the first visible evidence of reaction is 'map cracking' on the concrete's surface, which appears as a random network of fine cracks bounded by several larger cracks (see fig 1.13 in Appendix 1). However, this cracking pattern may be modified if the concrete is restrained by steel reinforcement in which case the cracks run parallel to the main bars. When the reaction is particularly active, a gel may be observed to be extruded from the cracks. The texture and colour of this gel may vary depending on the local reaction conditions. In practice the gel is often white in colour due to mixing with lime and carbonation. ASR may also become evident by distortions in the structure due to the volume changes of the concrete, resulting in misalignments or jamming of moving parts (e.g. bridge parapets or lockgates)(52).

The ASR process can be divided into two distinct phases; that of the reaction and that of the expansion.

The reaction takes place between the highly alkaline pore solution present in concrete's pores and ill-formed (non or crypto-crystalline) silica present in some aggregates. The pore solution consists almost entirely of sodium and potassium hydroxides(23,35), which produces an alkaline solution of pH value in excess of 13. The alkalinity of the pore solution is derived from Na^+ and K^+ present in the cement clinker, usually in the form of neutral sulphate salts. On hydration the sulphates which are readily soluble take part in a complex series of reactions with tricalcium aluminate (C_3A) and calcium hydroxide, from which ettringite (calcium sulpho-aluminate hydrate) is precipitated and the pore solution is enriched with sodium, potassium and hydroxyl ions. The alkaline solution then "attacks" the reactive silica constituent of the aggregate. The reactivity of the silica is dependant on its morphology and degree of crystal structure disorder(62). Hydrous forms of silica such as opal possess a highly disordered structure and are very reactive. Unstrained quartz, at the other extreme, has a well ordered structure and is normally unreactive. This reaction produces an amorphous gel.

The expansion phase which follows, simply involves the gel swelling as it imbibes water. The expanding gel which is confined by the surrounding concrete causes an internal pressure increase, until the tensile strength of the concrete is exceeded and cracking of the matrix occurs. Verbeck and Granlich(6) reported that the expansive alkali silicate substance could exist in several forms, solid, semi-solid or a liquid. All three forms were capable of imbibing water. Strubble and Diamond(19) also noted that the gel could exist in several forms. They observed using synthetic gels that as the solid gel took up water and started to exert a pressure, it became unstable and could convert rapidly into a liquid or sol. It was apparent from their work that the severity of expansion was dependant on the gel's composition, in particular its alkali to silica ratio. Therefore, two concurrent reactions are possible depending on the alkali concentration which will determine whether the gel will swell or not. High alkali concentrations resulting in the formation of expansive alkali silica complexes, while low alkali concentrations produce a solid, non expansive calcium alkali silica complex. These reactions are described overleaf(22);

Swelling type

SiO_2 + Alkali$^+$ + OH^- $\xrightarrow{H_2O}$ Alkali silicate hydrate

Non swelling type

Alkali silicate hydrate + $Ca(OH)_2$ $\xrightarrow{H_2O}$

Calcium (alkali) silicate hydrate +alkali$^+$ + OH^-

The actual process by which the gel absorbs water and expands has been debated since the 1940's. At present the water uptake mechanism of the gel is thought to be by direct sorption or imbibition.(6,53-55) The imbibition process is similar to that of the originally suggested osmotic cell mechanism, the primary difference being the absence of a semi permeable membrane. The regions of different chemical potential are then separated by the gel itself and its insolubility in the liquid.(55)

Water is absorbed into the silica gel but silica gels and ill crystalline silicas due to their rigid cross linked framework, are only able to take up limited quantities of water. This would not be able to provide sufficient swelling capacity to disrupt the concrete. That these gels are able to provide extensive swelling capacity and disrupt concrete may be explained by the alkaline environment provided by the concrete pore solution. In the alkaline environment, hydroxyl ions are imbibed with the initial water intake. These ions attack some of the strong Si-O-Si restraining linkages and loosens the rigid framework thus allowing more water and hydroxyl ions to be imbibed resulting in further swelling. This process continues to break down the rigid framework, working towards the interior of the silica and the resulting imbibition continues enabling the swelling pressure exerted to exceed the tensile strength of the concrete(55). A diagramatic representation of the framework breakdown as proposed by Iler(74) is shown in Figure 1.2.

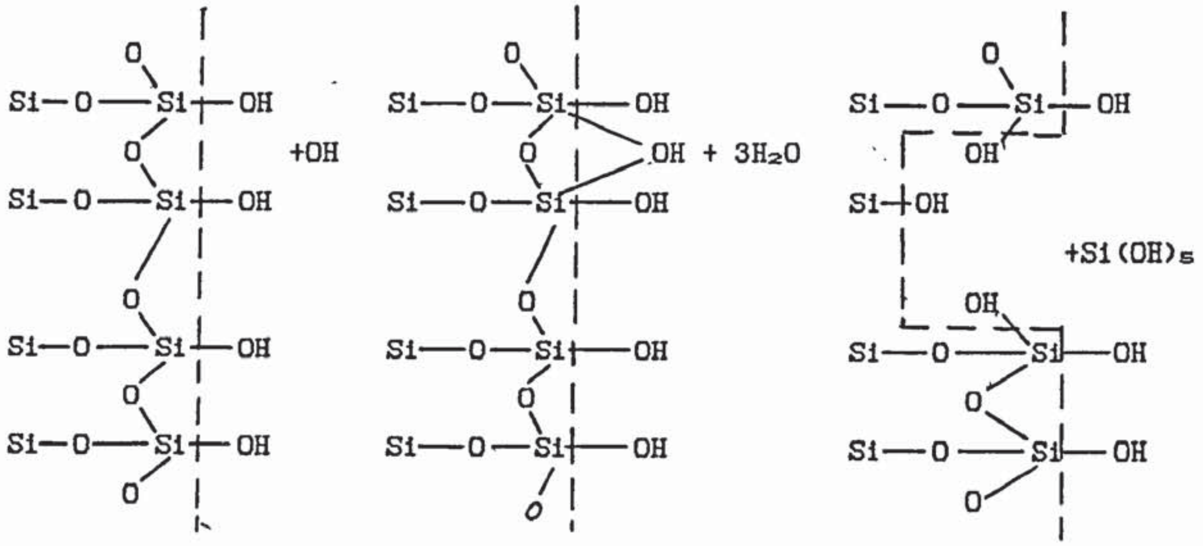


Figure 1.2 Mechanism of dissolution of silica in water by hydroxyl attack proposed by Iler(74). Dotted line represents the interface between silica and water.

Powers and Steinour(8), Diamond(56) and Gillot(53) have reported that, in practice, the cracking in concrete is primarily due to the solid swelling of the alkali silicate complex formed on the surface of the reactive aggregate.

Research work into ASR and its mechanism is reasonably difficult due to the large combination of factors which are able to initiate, accelerate or retard the reaction. The problem is further complicated as these factors are not independent of each other and may mutually have a strengthening or weakening effect on a combination of any given variables. This interdependence may give rise to a pessimum, which is the maximum expansion experienced when only one factor is varied. Pessima have been determined for many variables(18-21). However, it should be noted that pessima which occur for individual factors are not constant and move with the influence of other factors. This complex interelationship between pessima and the interactive variables makes extrapolation and cross referencing of empirical data provided by various workers difficult. Experimental results from expansive specimens usually only apply to the described mix reported as in that particular work so general conclusions cannot be drawn.

1.4 ASR - Reducing the Risk

The three components required for expansion due to ASR are:

1. An amount of reactive silica to be available in the aggregate.
2. Sufficient alkali present in the cement.
3. Moisture - imbibed by the gel to create expansion.

If any one of these conditions is not fulfilled, then the reaction can not take place. As such most of the precautionary measures aim to reduce or eliminate one or more of the primary reactants. The other method of controlling expansion is to partially replace the Portland cement by a suitable mineral additive, such as pfa of gbfs. The following paragraphs briefly outline the problems associated with each of the preventive methods.

1.4.1 Aggregates

In the United Kingdom, the use of siliceous aggregates is widespread, with extensive deposits of flints, chert gravels and quartz sands which have all been found to be potentially reactive in other parts of the world. However, due to the relatively small number of isolated incidents of ASR outside the South West and Trent valley areas the risk of inducing ASR by using these types of aggregate is considered to be slight, unless the other reaction components are considered to be particularly severe. A form of reactive silica has been found to exist in some flints and cherts. The silica is usually present as a secondary mineral, filling cavities and fissures of igneous rocks or as coatings on sands and gravel particles. Only relatively small fractions of the aggregate need to be reactive to cause a disruptive effect. Reactive silica may be present in either fine or coarse aggregate, although it is more commonly found in the fine aggregate.

If the quality of aggregate is doubted, its potential reactivity may be tested. The two most commonly used methods are: (i) ASTM C289-81 (57), the chemical test, which provides rapid results and grades the aggregate as being innocuous, potentially deleterious or deleterious. The test is described in greater detail in 3.2. (ii) ASTM C227-81 (58), the mortar bar test which is at present is considered to be fairly reliable although does not appear to be suited to British aggregates. The test involves simply measuring the increase in the length of mortar prisms (25 x 25 x 285 mm) cured under prescribed conditions. This test enables specific cement - aggregate combinations to be tested, which may take into account any pessima effects, but it does require considerable times unless cured at an elevated temperature.

Several other tests have been devised for aggregates around the world, but these seem to be used mainly by their developers and do not have widespread use. At present the British Standards Institute are developing a test which will be more suited to British aggregates. Petrographic examination provides the only conclusive evidence that aggregates suffering from ASR.

In Great Britain, for the majority of cases a rudimentary consideration of the aggregate(60) will be sufficient. Given the present number of occurences, difficulties with testing British aggregates and the cost of importing aggregate from alternative sources, extensive testing of aggregates is not appropriate. In all but the most severe cases it would seem unlikely that changing the aggregate would represent an economic option and that precautions against ASR must be achieved by implementing some other precautionary measure.

1.4.2 Cements

The second major component required for ASR is sufficient alkali. The reaction is unlikely to occur if the quantity of alkali ions in the pore solution is limited. Both potassium and sodium hydroxides are capable of attacking the silica portion of the aggregate. Therefore it is convenient to express the total alkali present in the cement as an equivalent sodium oxide content. This takes into account the potassium proportion of the alkali present and is calculated by(61);

$$Na_2O\ \%\ \text{equivalent} = Na_2O\ \% + (0.658 \times K_2O\ \%)$$

Since the alkalis present in the pore solution are principally derived from the cement component of the concrete, there are essentially two methods available by which the alkali contribution may be reduced. The first is by the limitation of the actual alkali level of the cement used, i.e. use of a low alkali cement. This is generally considered to be a cement having an Na_2O equivalent below 0.6 %. Cement manufactured in Britain typically varies in alkali content between 0.4 and 1 % equivalent Na_2O, with a national average (weighted production tonnage) of 0.6 %. The actual alkali level of cement produced at each factory fluctuates slightly over monthly/daily periods(51).

The second method of reducing the alkali present is to limit the total quantity of alkali present in the concrete. This method provides greater flexibility than the former method in that it takes account of not only the alkali level of the cement but also the cement content of the mix. It also allows other potential sources of alkali such as aggregates, deicing salts, etc to be taken into account. In Great Britain, a safe upper limit of 3 Kg of equivalent Na_2O per cubic metre of concrete is now accepted. The alkali content may be calculated(51);

$$A = C \times \frac{a}{100}$$

<u>where</u> A Alkali content of concrete ($Kg\ Na_2O/m^3$)

C Maximum cement content (Kg/m^3)

a Alkali content of the cement (% Na_2O equivalent)

A simple solution to the problem of ASR would be to manufacture cements low in alkali in the first instance. However, this is not easily accomplished, as virtually all the raw materials and the firing process used in the manufacture of the cement contribute alkalis. In the past, traditionally coal-fired kilns limited the quantity of alkalis in the cement by volatilizing the excess alkalis from the raw materials and venting into the atmosphere along with the exhaust gases and dust. The practice is no longer acceptable due to the joint pressure of economics and environmental concern so currently all the particulate materials (alkali rich dust) are electrostatically removed from the waste gases before discharge into the atmosphere. These large quantities of waste dust, which are essentially finely divided raw materials are returned to the raw feed circuit and inevitably the ever increasing alkali content of the kiln charge due to this returning process becomes a problem(62). This can be overcome by burning high sulphur content fuel, this results in the formation of alkali sulphates which require relatively high temperatures before they vaporize, as a consequence a greater proportion of the alkalis remain in the clinker and pass out of the kiln with it. This results in clinker with higher alkali contents.

In Britain, cement manufacture has used large rotary kilns to fire the cement clinker, as in most other places in the world. As energy and hence production costs continue to rise the trend for the future will be to use more energy-efficient furnaces in an attempt to reduce the cost of producing cement. Barneyback(39) in 1983 reviewed 3 general kiln arrangements which were currently favoured in the United States to help in reducing energy costs. All the systems involved the use of exhaust gases to preheat the raw material feed. While all the systems significantly increase the fuel efficiency, the alkali content of the cement clinker is also increased. Some reduction in the alkali content was achieved by drawing off dust at selective points along the process. However, it does seem that increases in the alkali content of cements are a normal consequence of increased energy efficiency in production. It is therefore unlikely that a significant reduction in the alkali content of cement can be expected in the near future and other methods of avoiding ASR are liable to become more attractive.

1.4.3 Environment

The third component required for ASR expansion is moisture, which in practice, may be derived from environmental sources such as rain, ground water or heavy condensation. It has been reported(18,81) that concrete maintained in a dry state will not suffer from ASR, even though it may contain reactive aggregate. Utilizing this concept the risk of ASR may be reduced if care is taken in the design of the structure. This precaution should be implemented both at the design stage by the avoidence of ponding or water build up adjacent to any concrete surface and while the structure is in service, by maintainance of drainage channels, weep holes, etc to ensure water is able to escape from the structure.

The temperature of the environment may also influence the rate of which the reaction occurs. Gudmundsson(15) determined that the reaction stopped at 10°C and provided maximum expansion at 38°C. This phenonomen has been used by many workers to accelerate the testing of expansive mortar bars. There is also some evidence to suggest that cyclic heating and cooling can also accelerate the reaction. The environment may also be able to increase the alkali concentration and possibly initiate or increase ASR. These increases are suggested to occur by two methods. the first is by alkali migration(63), this occurs in concrete specimens confined in water, but having one surface free through which the water may evaporate. It is suggested that the water passing through the structure absorbs and carries alkali salts to the place of evaporation or the free surface, the evaporation site then resulting in a localized alkali concentration. The second method of alkali increase involves the addition of alkalis from external sources, such as admixtures applied during mixing or from sea-dredged aggregates, or deicing salts introduced in the form of sodium chloride. Although opinions are divided or the extent of alkalis likely to be introduced by either method, both mechanisms have shown to increase the hydroxyl ion concentration of the pore solution under laboratory conditions(63,64). If damage from ASR is anticipated then these factors should not be ignored.

1.4.4 Blended Cements

Blended cements have also been used to successfully control or reduce the risk of ASR. The blend involves replacing a proportion of the Portland cement by a suitable hydraulic or pozzolanic* material. The mechanisms by which blended cements act to reduce ASR are considerably more complex than the precautions aimed at reducing or removing one of the primary reactants. The mechanism is thought to involve either dilution of the cements alkalis and/or increasing the fineness of the cement matrix microstructure.

Many pozzolanic materials have been found to be suitable for blending with the cement. These include burnt rice husk, volume ash and burnt clay all of which are particularly useful as cement extenders in the third world. The project, however, will only review the three most commonly utilized replacement materials, which are microsilica, pulverized fuel ash and ground blastfurnace slag.

1.4.4.1 Microsilica

Microsilica or silica fume is a by-product from the manufacture of silicon and ferrosilicon alloys. Silica fume consists essentially of very small spheres of pure silica in noncrystalline form, producing a specific surface of approximately 25,000 m^2/kg . Due to the controlled combustion the mineralogical composition does not vary greatly.

In work carried out by Page and Vennesland(37) silica fume was used to replace a high alkali Portland cement (1.19 % Na_2O equivalent) by 10,20 and 30 %. The hydroxyl ion concentrations of the cement paste's pore solution were reduced by levels which were greatly in excess of those expected by an inert diluent. When 30 % silica fume was used, the pore solution alkali concentration was reduced to a level below a saturated calcium hydroxide solution. Glasser and Marr(38) also found that silica fume was a very effective alkali diluent. They accounted for its action by proposing that the silica helped to produce a low calcium to silica ratio C-S-H phase, which had the ability to remove a greater quantity of alkali ions from the pore solution. The actual mechanism of removal is uncertain, although they suggested that this might occur by precipitation of an insoluble alkali containing compound or by direct absorption of the alkali by the low calcium C-S-H.

* Note

ASTM C 618(65) defines a pozzolan as 'siliceous or siliceous and aluminous material which itself possesses little or no cementitious value but in a finely divided form and in the presence of moisture, chemically reacts with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties'.

Silica fume is presently being produced at the rate of 1.1 million tonnes per year. Although research has shown the effectiveness of its use, it has had only limited use in practice outside Scandinavia.

1.4.4.2 Pulverized Fuel Ash

World production of flyash is currently approaching 400 million tonnes per year (which represents approximately 50 % of world cement production). The material consists of ash particles which have been precipitated electrostatically from the exhaust fumes of coal burning power stations. The particles are glassy spheres ranging in size from 1μm to 100μm but the majority are under 20μm. The glassy spheres maybe solid, hollow (cenospheres) or hollow filled with similar spheres (plerospheres). The ashes's physical and chemical properties depend on the type of coal burnt and the efficiency of burning. Many workers(23,28,67) have explored the properties of ashes made from different types of coal and burning processes.

Flyashes may be characterized by their material properties. Generally this means being divided into high or low calcium content ashes. This classification approximates to that made by ASTM C 618(68) which differentiates the calcium content indirectly, as described below;

Class C ashes; (high calcium content) requires a minimum content of 50 % non calcium oxides.

Class F ashes; (low calcium content) requires a minimum content of 70 % non calcium oxides.

The class C ashes are readily activated by their own lime content and/or by the calcium hydroxide released during the hydration of Portland cement. These high calcium ashes are usually derived from burning lignite and some bituminous coals, which produce ashes having a good pozzolanicity index. The class F ashes are usually derived from burning of bituminous coals. Due to the high proportion of alumina and silica, the ash spheres are essentially made up of alumino silicate glass. This makes class F ashes relatively non-reactive. Usually these pfa's are activated by the alkalis released by the cement hydration and therefore have a lower degree pozzolanicity.

There is some controversy over the effectiveness of pfa as a preventative measure against ASR. This is principally because some ashes may contain relatively high quantities of alkali (up to 4.6 % Na_2O equivalent in U.K ashes). The role of this alkali is not fully understood, but it is thought that most of the alkali is "locked up" in the glassy structure, the ashes effectively acting as an inert filler diluting the cements alkalis. Many workers(37,39,40) have shown the benefit of ash inclusion as a preventative measure to ASR. In practice, if 30 % of the Portland cement is replaced by a pfa then this is usually sufficient protection against ASR.

The reaction products in flyash are similar to those of Portland cement, but the rate of hydration is much slower. Pfa may take upto 28 days before it starts to hydrate and many months before fully hydrated. The relative quantities and composition of reaction products and their physical structure will be dictated by the glassy structure of the ash particles. The ultimate rate at which the ash hydrates will be dependent on the compostion of the blended Portland cement, the mineral composition and particle size of the ash, reaction temperature and ionic concentration of the pore solution(67).

1.4.4.3 Blast Furnace Slag

The cementitious properties of ground blastfurnace slag have been known for at least 100 years. The slag, a waste product from the manufacture of pig iron, may be mixed with limestone and used as a raw material for the manufacture of Portland cement or interground with ready made cement to form a blended cement. When the substition level exceeds 50 % of the Portland cement the risk of ASR occurrence is significantly reduced.

The material has a similar oxide composition to Portland cement, but the relative quantites of constituent oxides and physical structure of the slag varies with the manufacturing process and the method used to cool the molten slag. Essentially there are two methods of producing slag for use as a cement additive. The first method cools the molten slag by quenching in water. This produces granulated slag. The second method quenches the molten slag with a combination of water and air which produces a pellitized slag. Both methods produce materials containing lime, magnesia, silica and alumina which are held in a non crystalline or glassy state. The former method produces a slag with a greater glass content. After cooling the slag is ground down to a powder of approximate fineness 400 - 600 m^2/kg Blaine surface area. When ground the material has both cementitious and pozzolanic properties(67).

Ground slags and high calcium pfa share similar properties. They are both essentially glassy (approximately 90 %), have similar mineralogical composition and reactivity of glass. The major difference between the ash and slag is that high calcium ashes are readily reactive and may start to hydrate almost immediately, where as gbfs's generally are slower to hydrate and may need to be "activated" by the alkalis produced by the cement's hydration (approximately 3 days). Alternatively, the slower slag proportion of blended cements may be activated or have their hydration accelerated by a number of other methods so the reduced strength development of the slag blended cement may be overcome. These methods involve the use of chemical activators such as added alkali sulphates, grinding the slag grains to an increased fineness or using elevated curing temperature.

Like pfa, slags may also contain comparatively high total alkali contents which are combined within the glassy structure. This alkali as with pfa's does not appear to find its way into the pore solution. The ability of slags to prevent ASR is thought to be based on alkali dilution and/or a finer microstructure, although the importance of each is debated. Bakker(22) and other workers(42,43) have shown that slag blended cements produced a greater quantity and a more compact CSH gel. The increased fineness of texture reduced the permeability of slag cement concrete to water and alkali movement. Glasser and Marr(38) report that the role of slag is broadly neutral in respect to alkali ion removal from the pore solution, and would require large quantities of low alkali slags to remove significant quantities of alkali ions from solution.

1.5 Purpose of Investigation

It is well established that ASR may be controlled if a proportion of the Portland cement is substituted by a suitable hydraulic or pozzolanic material. This replacement may result in a dilution of the cement alkalis and/or a microstructure of increased fineness. Each factor has been independently proved to be an effective method of controlling ASR. In this project it has been attempted to identify the factors which influence the relative importance of each mechanism in the overall suppression of the reaction by blended cements.

This has been principally achieved by the chemical analysis of pore solutions extracted from specimens of hardened cement pastes, mortars and concretes. The technique used to express this pore solution was developed approximately ten years ago and provides a method by which the alkali content of the hardened specimen may be measured. Relatively few attempts to use this technique to study pore solution alkalis in relation to ASR have been reported. Therefore, an opportunity to use expressed pore solution to measure alkali contents and the possibility that it may be used to elucidate the effects of blended cements in the control of ASR existed. From this the main objectives of the study were specified as being;

1. To determine the influence of the pore solution alkali concentration on expansion due to ASR.
2. To determine the relationship between the alkali content of the cement and the pore solution alkali concentration of cement pastes, mortars and concretes.
3. To investigate the effect on the pore solution composition when the alkali contents of blended cement (cement/pfa and cement/slag) combinations were varied.
4. To establish the ability of cements to complex alkali salts, from external sources, and assess the possibility whether this reaction may be able to exacerbate ASR.

5. To undertake a limited study to identify the factors which determine the ability of blended cements to control ASR by reduced ionic mobility.

1.6 Plan of Presentation

Chapter one reviews ASR as a subject, outlining the historical background, the mechanism by which the reaction proceeds and the measures available to designers of new structures to reduce the risk of ASR occurrence

Chapter two details the materials and experimental procedures used in this work.

Each of the following experimental chapters is presented using a common format consisting of an introduction to the work carried out, the previous work in that area reported by other researchers. Then the experimental work is described.
Chapter three describes the ability of a range of blended cements to control ASR expansion at predetermined simulated pore solution alkali concentrations and presents a limited study relating the observed control to the permeability of the material.

Chapter four studies the influence of the cements' alkalis on the pore solution composition.

Chapter five describes the effects on the pore solution composition when a range of cements of varying alkali content are partially substituted by reference replacement materials.

Chapter six compares the pore solution compositions produced when a range of pfa's and gbfs's of various alkali content were used to replace a reference cement.

Chapter seven describes the effect that added alkali salts had on the cement pastes pore solution composition.

Chapter eight presents the general conclusions and recommendations for future work.

CHAPTER 2

Experimental Materials and Techniques

2.1 Materials

2.1.1 Cements

A series of five Portland cements was used to produce the cement pastes, mortars and concretes in this study. These cements were selected for their natural alkali content. All the cements were produced and are commercially available in the United Kingdom. Although all the cements were of ordinary quality, cement A was a white cement.

Table 2.1 in Appendix 2 details the composition of each cement as a percentage by weight of the constituent oxides. The potential compound composition of each cement has been calculated using Bogue's(75) equations and results of the calculations are shown in Table 2.2. It should be noted that this method may underestimate the C_3S content and overestimate the C_2S(76).

2.1.2 Pulverized Fuel Ashes

A series of five pulverized fuel ashes were selected for use as cement replacement materials. The ashes were chosen primarily for their alkali content and secondly for their physical fineness. All five ashes were produced and are commercially available in the United Kingdom.

The chemical composition of the ashes are shown in Table 2.3 by the percentage weight of the constituent oxides. In addition, ashes 2,3, 4 and 5 were tested to B.S 3892. Part 2(77) by the Building Research Station and the results of these tests together with a general description of alkalinity and fineness of the ashes are shown in Table 2.4 in Appendix 2.

2.1.3 Ground blastfurnace slags

In addition to the pulverized fuel ashes, three blastfurnace slags were also used to replace the cements. The slags were again selected to provide a range of alkali contents. All three slags are marketed in the United Kingdom, but only slag 1 was produced in this country. Table 2.5 details the chemical composition expressed as percentages by weight of the constituent oxides, together with the method of production of each slag.

2.1.4 Aggregates

Three types of aggregate were used to produce the mortars and concretes used in this study. The non expansive specimens were produced using a Cheddar limestone fine aggregate and a crushed limestone coarse aggregate, both of which were free from any reactive silica. In addition to the two non reactive aggregates, Beltane opal a standard reactive aggregate was used to produce the expansive mortar specimens used in Chapter three. Sieve analyses of these three aggregates are detailed in Tables 2.6, 2.7 and 2.8 in Appendix 2.

Beltane opal was selected as the reactive aggregate as published data indicated that the aggregate was likely to progress through its expansion process within a reasonable time scale and provide sufficiently large physical expansions which could be readily measured. The wide experience of the behaviour of this aggregate in previous researches(39,40,78) proved to be useful in designing experimental mixes. Although no independent chemical analysis was available for the actual sample of opal used, it is thought that the composition was unlikely to be significantly different from those shown in Tables 2.9 which were obtained for a sample that originated from the same source and stock as that used in this study.(39,79)

Beltane opal is a predominantly siliceous and amorphous material, which accounts for its highly reactive potential. Previous workers(39) have identified some crystalline structures present, the quantity and type of structure appear to depend on the relative geological formation process. An X ray diffraction analysis of the opal used in this work as shown in

Figure 2.1 was carried out to ascertain the presence of crystalline phases within the material. The Geological Sciences department of Aston University provided valuable assistance in interpretation of the recorded X ray trace. The peaks of X ray intensity although well pronounced were relatively small which indicated that the material was predominantly amorphous but contained the following crystalline minerals. Each is referenced to the Joint Committee on Powder Diffraction Studies(80) (JCPDS);

Silicon dioxide alpha cristobalite	JCPDS ref 11 - 0695
Silicon dioxide alpha tridymite	JCPDS ref 18 - 1170
Silicon dioxide alpha quartz	JCPDS ref 05 - 590

Barneyback(39) carried out extensive examinations of the mineral composition of samples of Beltane opal. He reported the same mineral formations as shown above together with Alunite JCPDS ref 14 - 0136. From his analysis, Barneyback concluded that the Beltane Opal primarily consists of amorphous opal with some tridymite twins, quartz, feldspars microlites, dirty glass and some other minor amounts of unidentifiable material.

2.2 Experimental Techniques

2.2.1 Mixing Procedure

The mix components were batched by weight and thoroughly dry mixed by mechanical mixer to ensure complete mixing and an even distribution of the components before the mixing water was added. For blended cement specimens the cement and its replacement material after batching were hand mixed by trowel and then twice passed through a 300 micron sieve to ensure a homogeneous cementitious component before mixing with any other mix constituents.

Once the dry components were evenly distributed, the mixing water was added. Deionised water only was used for this purpose. Mixing was continued for a further ten minutes, with a short break at the mid period to ensure no material was left unmixed or stuck to the sides of the mixing vessel (removed by means of a hand held trowel). On completion, the mix was transferred to the appropriate specimen moulds and cured for 24 hours at 20°C. The specimens were then demoulded and individually marked for future identification and removed to be stored under predetermined curing regimes.

2.2.2 Pore Water Expression

The pore water, the unbound water within the pores of the hydrated cement structure was extracted from hardened paste, mortar and concrete specimens by subjecting them to high pressures. The specimens used for pore solution expression were cast into sealed plastic moulds, each 75mm long by 49mm diameter. Cured specimens ready for expression were demoulded immediately prior to testing and broken into small pieces (approximately passing through a 12mm sieve) before loading into the pore solution expression apparatus. The construction of the press is similar to that first described by Longuet, Burglen and Zelwer(27) and shown in Figure 2.2 in the text and Figures 1.4 and 1.5 in Appendix 1.

The sample was contained within a cylindrical vessel and subjected to pressure created by a free moving piston which was loaded by a hydraulic press. The load applied was increased at the rate of approximately 1 MPa per second, upto a maximum pressure of 350 MPa. This pressure was normally maintained for 15 minutes, mixes which had low water contents ratio usually required longer periods under load. The expressed pore fluid was drawn off under slight vacuum, created by a plastic syringe via a fluid drain provided in the base plate. This method also avoided undue exposure of the pore solution to air. The expressed solution was then stored in sealed plastic vials until analysed.

Although the pore solution expressed represents only a small fraction of the total evaporable water present in the specimen it is a reasonably accurate representation of the specimen. This correlation was determined by experimental work at Aston University(81) by analysis of the expressed pore solution from previously equilibrated specimens. However, here is some evidence to suggest that the magnitude and duration of the applied pressure may have a small influence on the composition of the expressed liquid(82).

2.2.3 Analysis of Expressed Solution

The expressed pore solutions were allowed to stand up to three hours in their air tight vials. This allowed any suspended cement particles, if present to settle out before analysis commenced. The solutions were analysed for hydroxyl, sodium and potassium ion concentrations, together with the free chloride ions present in certain samples. The calcium content of the pore solutions obtained from early specimens was determined by titration against Ethylenediaminetetra-acetic acid (EDTA). However, the concentration of calcium was barely detectable and the determination of this ionic species was discontinued.

The hydroxyl ion concentration was measured by acid base titration. A 0.1 ml aliquot of the expressed pore solution was diluted with 0.9 mls of deionised water and titrated against 0.01 M nitric acid to the end point of phenolphthalein This indicator was considered to provide a reasonably well defined end point (pH range 8.2 to 10) for the pore solutions expressed. The quantity of acid required was measured by a 10 ml burette (with 0.02 ml divisions) which was suitable for the entire range of specimens used in this study.

Sodium and potassium concentrations were determined by flame photometry. Duplicate specimens from each pore solution were produced from a 0.1 ml pore solution aliquot in 50 ml of deionised water. This produced a concentration which could be detected with reasonable sensitivity by the photometer, which was calibrated according to the specimens under test. A series of calibration standards equivalent to 5, 10, 15, 20, 25, 30, 50 and 60 parts per million (ppm) were used for this purpose. The calibration standards were made from a master standard equivalent to 500 ppm, produced from analytical grade sodium and potassium chlorides. Tests to ensure that the use of the twin standards in the same solution was not the cause of inaccuracies due to interference were carried out prior to the commencement of the test programme.

The free chloride ion concentration of the expressed pore solution was determined by a colorimetric method(83), using a Beckman Model 24 double beam spectrophotometer. Colorimetric reagents in the form of 2 ml of 0.25 M ferric ammonium sulphate ($Fe\ (NH_4)(SO_4)_2,\ 12H_2O$) in 9 M nitric acid and 2 ml of saturated mercuric thiocyanate in absolute ethanol were added to a 0.1ml aliquot of pore solution which had been diluted with 9.9 ml of deionised water. The solutions were allowed to stand for ten minutes while the colour developed. The colour intensity was related to the chloride ion concentration, as a result of the chloride ions displacing the thiocyanate ions forming a coloured complex with the ferric ions. The reaction is described below.

$$2\ Cl^- + Hg(SCN)_2 + 2Fe^{3+} \rightarrow Hg\ Cl_2 + 2(Fe(SCN))^{2+}$$ (83)

The spectrophotometer measured the absorption of light at specific wavelengths, in this case 460 nanometers as a beam of light was passed through a glass sample cell filled with the coloured solution. The difference in the light absorbed between a blank (clear) and test solution was proportional to the amount of chloride ions present. Using the Beer-Lambert law which states that

$$I_t = I_0 \,.\, 10^{-Ect}$$

where I_t Transmitted intensity
I_0 = Intensity of incident light
E = Molecule extinction Coeff.
C = Concentration of solution
t = thickness of solution

then for a constant path length, the intensity of a beam of monochromatic light is inversely proportional to the concentration of the absorbing substance it passes through(84). The molarities of the specimens under test were calculated using a callibration curve of standard chloride solutions against absorption.

Theoretically the sums of cations and anions detected in the pore solutions should balance. In practice, it was generally possible to balance the sums of ions to within a 5% tolerance. The imbalances were attributed to experimental errors which were probably due to the presence of suspended particulate materials in the sample and/or the higher concentration pore solutions lying off the linear part of the flame photometry scale.

2.2.4 Determination of Free and Bound Water

The determination of the quantity of the original mix water which has been either bound into the hydrating cement structures or is present as free water in the pores is essential to extract the most from the analytical ion concentration data. An estimate of the free water content provides a guide to the amount of solute in the pore solution. The ratio of the free to bound water also provides an indication as to the degree of hydration that has taken place. Previous workers(36,37) have measured the free water content by drying the specimen at 105°C until a constant weight is reached. The weight lost by the specimens, i.e. the evaporable water content was then assumed to be equal to the free water content. If the specimen was heated upto 950°C the weight lost approximated to the total water content of the sample. The division of free and bound water however, is not as readily differentiated as suggested by the method. Inevitably some of the bound water would be lost at 105°C from the calcium sulphoaluminates and the hexagonal tetracalcium aluminate(85). Taylor(86) in recently published work reported that a more accurate assessment of free and bound water may be made by measuring the weight loss of a crushed cement specimen stored at 18°C at 11 % RH. The figure he obtained by this method was consistent with the probable dehydration behaviour of the individual hydrated cement minerals. Taylor compared the bound water content for a 14 month old cement by both heating to 105°C and drying at 11% RH, and determined them as being 15 % and 22.8 % respectively.

The implications of these findings may result in the method used providing an overestimation of the actual free water content and thus the quantity of ions calculated to be in the pore solution. However, the 105°C method provides a consistent relative measure of free water contents between specimens and achieves a constant weight relatively quickly. As such the conclusions drawn from the observed trends should still be valid. The method used for the determination of the free water content will need to be closely examined before any further work is undertaken.

The actual procedure used for this work to estimate the free water content involved measuring the weight lost by a 3 gramme sample of hydrated, non compressed material. i.e. representative of specimens before pore solution extraction. The sample was fragmented, placed in a platinum crucible and heated until a constant weight was reached at 105°C. The weight loss was then related to the cement content of the mix and determined as grammes of water per gramme of unhydrated cement. The non evaporable water content was calculated arithmetically by subtracting the free water content from the total water content.

The method did have the advantage that inaccuracies due to sulphur components of slag blended cements which are released when heated to 950°C were avoided. An example of the calculations used to determine the free and bound water contents are shown below and based on Lambert's work(67).

For Cement Pastes

$$\text{Free water content} = \frac{W_o - W_{105}}{W_{950}} \times (100 - i + a)$$

$$\text{Bound Water content} = \frac{W_{105}\,(100 - i + a) - W_{950}\,(100 + a)}{W_{950}}$$

Where

W_o	Original mass of specimen
W_{105}	Mass of specimen at 105°C
W_{950}	Mass of specimen at 950°C
i	Loss on ignition (% g/g unhydrated cement)
a	Mass of admixtures.

For Cement Mortars and Concretes

Free water content

$$= \frac{\text{Mass of mix components (for 1grm of cement)} \times (W_o - W_{105})}{W_o}$$

Bound water content = Water Cement Ratio - Free Water Content.

Example

In a mortar mix having an aggregate to cement ratio of 2 and a water to cement ratio of 0.5. The mass of mix components required for 1 gramme of cement to be present would be 3.5 grammes. [1 part of cement + 2 parts of aggregate + 0.5 parts of water].

2.2.5 Pore Size Distribution Measurement

Mercury intrusion porosimetry (MIP) was used to measure the pore size distribution of hydrated cement mortar specimens. The technique involved forcing a non wetting liquid (mercury) into the pores of the specimen. The quantity of mercury that is forced into the pore at a given pressure may be used to calculate the pore diameter by means of the Washburn equation(88).

$$P = \frac{-4\gamma \cos\theta}{d}$$

Where:- P = the applied pressure (Pascals)
γ = surface tension of mercury (N/mm^2)
θ = contact angle between mercury and material (degrees)
d = pore diameter (microns).

The main criticisms of applying the MIP technique to cement pastes are that the pore size distributions are biased towards the coarser range of pores and the mercury may crush the fine pore structures at the higher pressures. MIP also may provide smaller diameter measurements for pores having a restricted entryway such as "ink bottle" shape or similar.

These types of pores are classified into a size equivalent of the maximum size of the entryway, which would be smaller than a true measure might show. Feldman(89) suggested that in blended cement specimens which have a finer structure the mercury could break into these "ink bottle" pores causing a partial collapse of the structure, although this was limited in ordinary Portland cements. Therefore in blended cements the pore size distribution of pore radii smaller than 10 nanometers should be interpreted cautiously (89), Diamond (90) concluded that the MIP technique provided a reasonably representative distribution between 1000 microns and 20 nanometers for ordinary Portland cements. The specimen drying technique also influences the contact angle of the mercury and account of this must be taken in the application of the Washburn equation.

The MIP technique was used to measure the pore size distribution of both plain and blended cement mortars. A Micromeritics Instrument Corporation model 900/910 porosimeter was used to determine the distribution of oven dried (105°C) specimens. Approximately 5 grammes of dried specimen was placed into a glass cell of known volume, the cell was then fitted into the porosimeter (as shown in fig 1.6 and 1.7 in Appendix 1) and the system evacuated to remove any absorbed vapour or gases. Mercury was introduced into the cell under vacuum. The pressure applied to the mercury was increased in a series of increments. At each pressure increase the mercury penetration value was recorded. Assuming a mercury contact angle of 117°(91). the pore diameter corresponding to that pressure was determined together with volume of similar sized pores. The data obtained have been plotted as the pore diameter against the cummulative volume (percentage by volume) using a logarithmic abscissa to display the large range in pore diameter sizes.

2.2.6 Steady State Diffusion Measurements of NaOH

This technique was used to measure the rate at which sodium and hydroxyl ions were able to diffuse through thin discs of cement paste. The discs were produced by carefully batching and mixing the cement paste components as described in 2.2.1. Special care was exercised during the filling of the moulds and their compaction to ensure no unmixed material or air bubbles became trapped in the matrix. The moulds used were sealable cylindrical containers 75 mm long by 49 mm diameter and were stored at 20°C for three days. At this age they were demoulded and cut into slices approximately 3 mm thick using a Metals Research Microslice 2 saw fitted with a 150 mm diamond tipped blade. The cut discs were lightly ground on either side using 600 grade abrasive paper to remove any burrs and then were visually checked for any imperfections or flaws. The discs were cured in a 0.035 molar sodium hydroxide solution in sealed containers at 20°C for 53 days. This solution equilibrated the specimen discs to the lower concentration side of the diffusion cell. The solution was changed periodically.

On reaching 56 days old, the specimen discs were set in the diffusion cell as shown in figure 2.3. The thickness of the disc and the volume of the solution in the cell were measured. The diffusion cells were maintained at 38°C for the duration of experiment by means of a water bath, as shown in figure 1.9 in appendix 1. The discs acted as a partition between two cells, one containing a sodium hydroxide solution of a high concentration and the other, a much lower concentration of the same solution. It was possible to find the diffusion coefficient of the "partition material" by keeping the unequal concentrations on either side of the disc effectively constant and measuring the ion flux entering the low concentration half of the cell. This technique has now been well established(93,94,95) and is based on Fick's first law of diffusion. (89)

$$J = -D \frac{dc}{dx}$$

Where:-

J = the amount of substance passing perpendicularly through a surface of unit area during unit time.

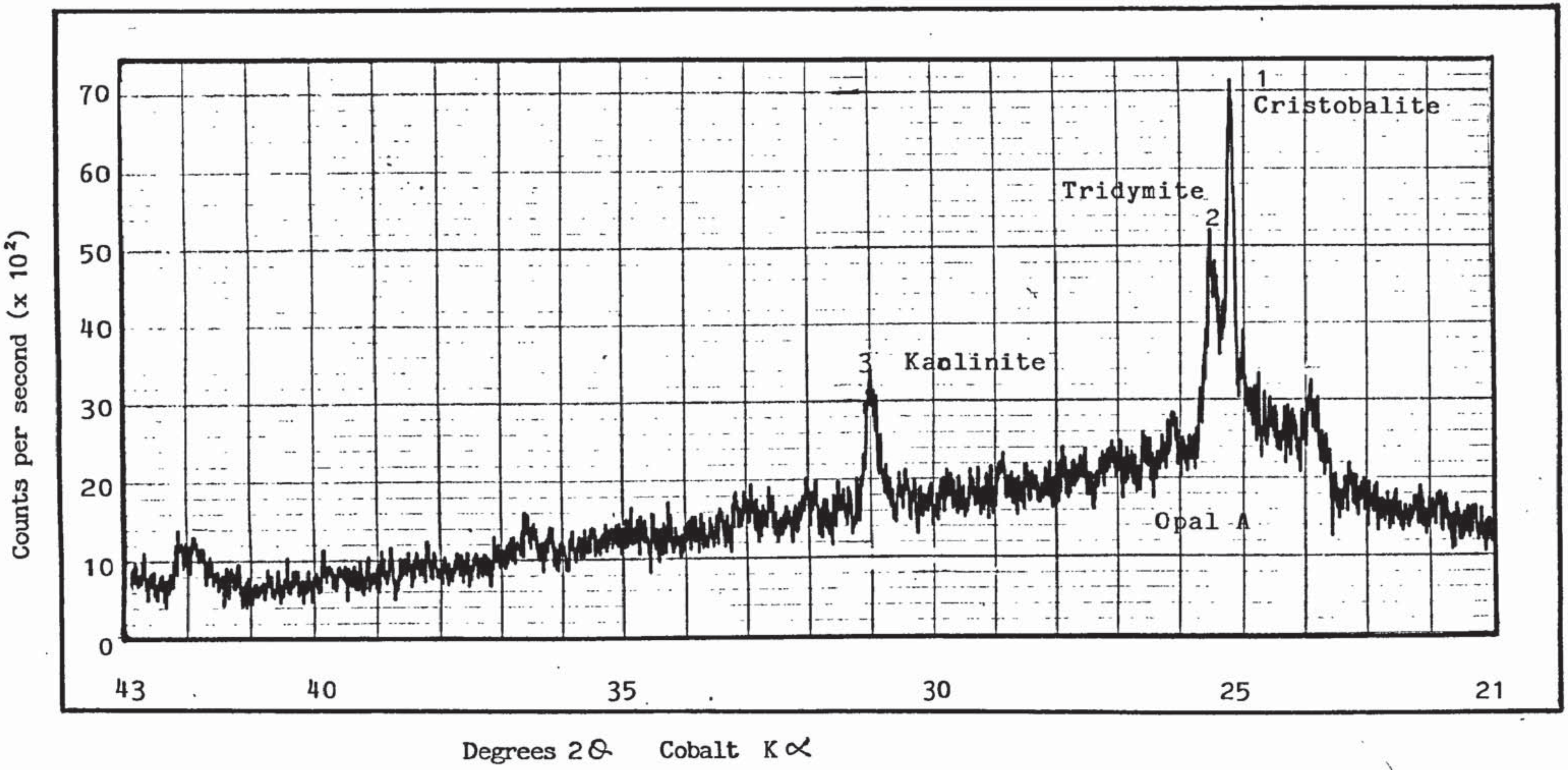
D = the diffusion coefficient

$\frac{dc}{dx}$ = the concentration gradient of the diffusing substance in the direction of diffusion.

The increase in ion concentration in the lower concentration half of the cell, although detectable was sufficiently small so as to be insignificant in the maintenance of the relative concentration difference. This concentration increase with time is linear and represents the amount of diffused substance per unit area of the disc, i.e. the flux, which is proportional to the diffusion coefficient. The concentration increase was monitored by periodically taking 0.1 ml alliquots of solution from the lower concentration solution and analysing for sodium by flame photometry and hydroxyl ions by acid-base titration.

This technique for determining diffusion coefficients has been critisized by some workers. Atkinson and Nickerson(96) were critical of the cell arrangement and thought that some osmotic flow of liquid from the low concentration half cell through the disc to the high concentration solution may result. They also thought that the calculated diffusion coefficients may be underestimated due to the porosity of the material. The coefficients do not represent the flux flowing through a cross sectional area of liquid, but that through the area of the medium. A further criticism leveled at this technique is that it is not representative of any real practical environment. However, the advantages of this technique, those of speed, its non destructive nature and small specimen requirement were considered to outweigh the disadvantages and justified its use to obtain diffusion coefficients suitable for comparison between various blended cement pastes.

FIG 2.1 X ray diffraction pattern for Beltane Opal



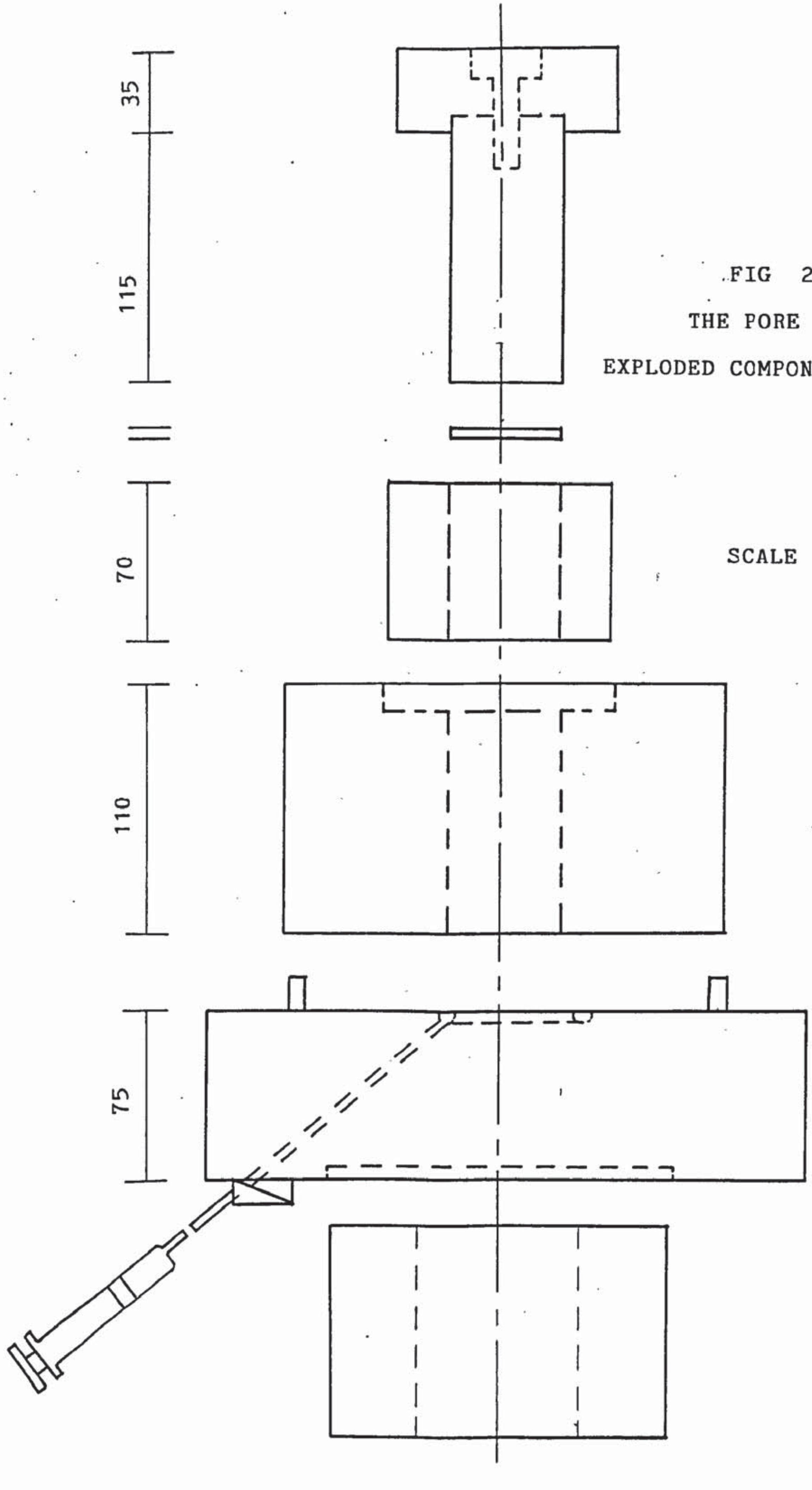


FIG 2.2

THE PORE PRESS

EXPLODED COMPONENT DIAGRAM

SCALE 1 : 2.5

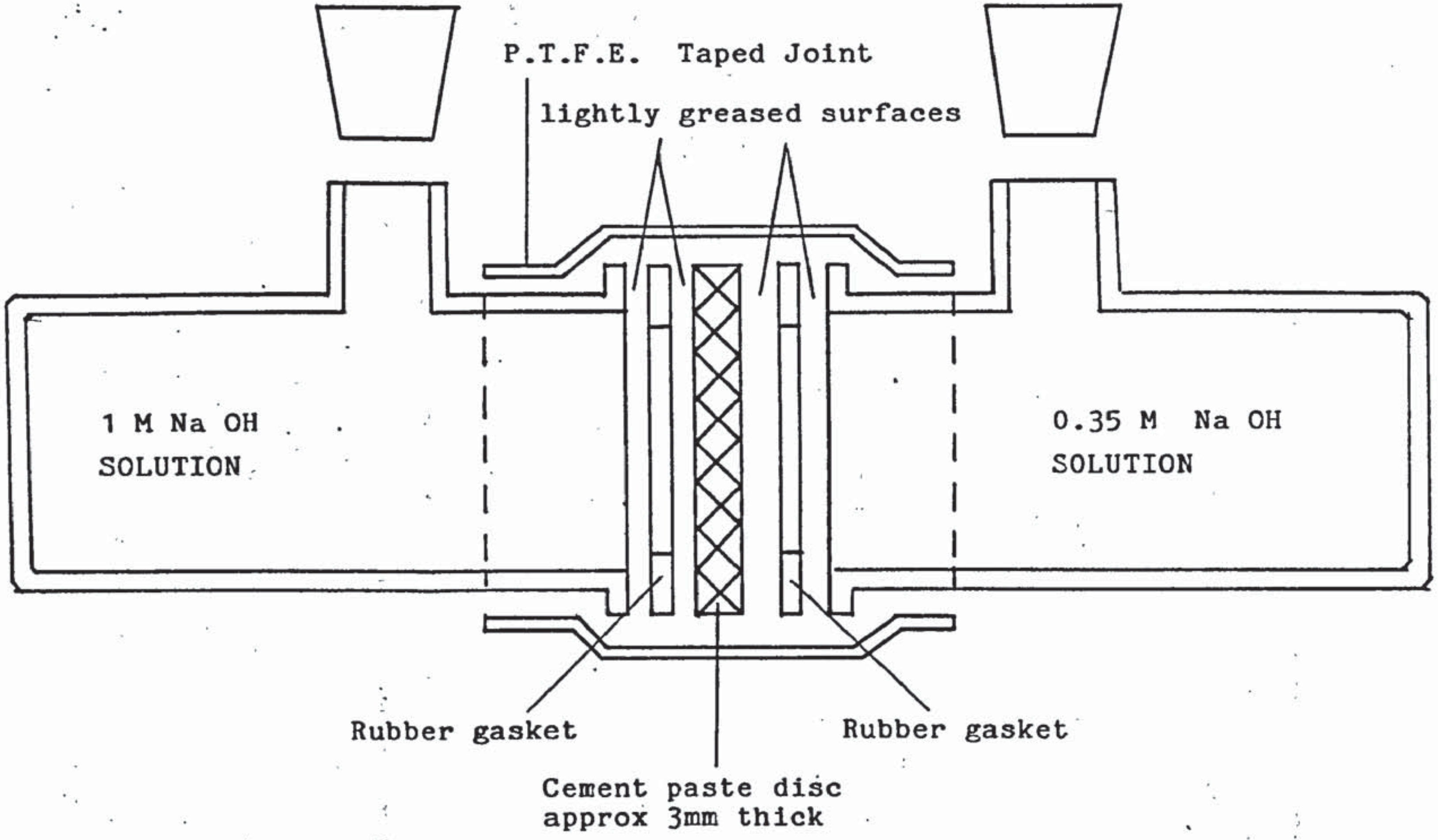


FIG. 2.3 EXPLODED SECTION THROUGH A DIFFUSION CELL

CHAPTER 3

The Control Exerted by Blended Cement Mortars

3.1 Introduction

Several workers have used expansive mortar bar techniques to demonstrate that specimens produced with high alkali cements generally expand to a greater extent than similar specimens made using lower alkali cements. Other groups of workers have independently shown using pore solution analysis that the alkali concentration of cement pastes and mortar pore solution are primarily dependent on the alkali content of the cement used. However, little work has been reported relating the pore solution concentration directly to the expansion.

The work in this chapter has attempted to correlate the pore solution alkali concentration directly to the rate of expansion, by the use of reactive mortar prisms subjected to a range of artifical simulated pore solutions of known concentration. In addition, the ability of various blended cements to control expansion was assessed and the existence of a pore solution alkali concentration expansion threshold was explored. The control of ASR expansion by the blended cements was then related to the permeability of the material in a limited study.

3.2 Previous Work

Cement mortar bar expansion measurements and the influence of cement alkali content on the pore solution composition have been reported on in many contexts quite extensively. This work is reviewed in other chapters of the thesis. The discussion of previous work in this chapter has been confined to that work published in relation to the enhancement of cements' natural alkali content by design and the microstructure/permeability of blended cements. The inclusion of additional alkalis has been used in the study of ASR generally to promote rapid expansion of mortar/concrete specimens or to determine the potential reactivity of aggregates.

ASTM C289(67) uses an alkaline solution to provide a method for assessing the potential reactivity of aggregates. The specimen aggregate (crushed to between 150 and 300μm in size) is reacted with a 1 M sodium hydroxide solution at 80°C for 24 hours. The quantity of silica dissolved into the solution is determined together with the reduction of the solution's alkalinity, from these measurements the aggregate may be classified as being innocuous, potentially deleterious or deleterious. Knudsen(97) developed a similar technique to assess the reactive silica content of aggregates. In this method the dissolution of the silica was measured by its chemical shrinkage using a 10 M sodium hydroxide solution at 50°C. The technique was used to measure the reactive silica content of aggregates known to be reactive. Knudsen reported good correlation between the quantity of silica determined and expansions measured for 8 week old mortar bar specimens.

The addition of alkalis to cement mortars and concretes has also been used to enhance natural alkali contents and thus induce rapid ASR expansion. Various methods of adding the alkali have been reported. Several workers(98,99,100) from Japan have used combinations of alkali addition and autoclaving to increase the rate of ASR. Each method devised involved storage at an elevated temperature and generally produced results within 3 to 5 days. Nixon and Bollinghaus(102) increased the alkali content of mortar bar specimens by dissolving quantities of potassium hydroxide in the mixing water to produce a total equivalent soda content of 2.4% (14.2 kgs Na_2O/m^3 concrete). The specimens were then stored at 38°C. The considerable alkali content of the specimens was sufficient to initiate expansion in aggregates which were known to be reactive in practice but had previously proved difficult to test successfully under laboratory conditions.

An interesting study was undertaken by Tang Ming Shu and Han Su Fen(101) who used an alkali solution and expansion measurements to model the reaction kinetics of ASR. The length changes of 10 x 10 x 40 mm mortar bars made with a high alkali cement and a variety of aggregates were measured. The mortar bars were cured for 24 hours, then stored in a 10% potassium hydroxide solution. Their data demonstrated that the expansion process typically progressed through three stages, as shown in Figure 3.1

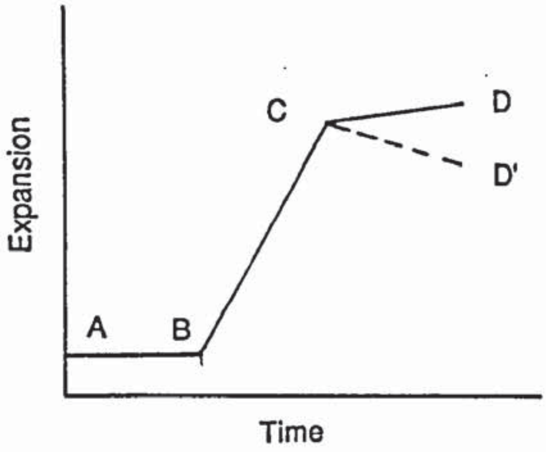


Fig 3.1 Schematic figure of the ASR process from reference 101.

From microscopic observations they found ASR to be taking place during the dormant period (AB). Once the expansive stresses of the reaction were sufficient to overcome the physical strength of the mortar the specimen expanded (BC) and a linear dependence on time was observed. That the relationship was linear rather parabolic as expected from a liquid/solid reaction was attributed to the disintegration of the aggregate producing new enlarged reactive surfaces. The constant expansion rate tailed off during the final period (CD, CD') due to aggregate exhaustion and/or inefficient conversion of expansive stresses through the cracked specimen into length change. The expansions of specimens were determined as functions of both time and temperature and were found to be predicted by the Arrhenius equation;

$K = K_o \exp(^{-E}/RT)$ where

K	Rate constant
K_o	Frequency factor
E	Activation energy
R	Gas constant
T	Absolute temperature.

However, the correlation for each aggregate only existed over a relatively short temperature range and each aggregate had its own temperature related limit, above which expansion would not occur. This data was used to calculate activation energies for the aggregates tested with the objective of differentiating reactive types from non reactive. They concluded that their method provided a better indication of the aggregates' likely performance than that which could be provided by relying solely on the expansion value of mortar bars cured at only one temperature.

Hobbs(78,103) modelled the ASR based on expansion measurements from various mortar mixes. The original simple model, which proposed that if the pore solution hydroxyl ion concentration was sufficient to maintain ASR then the rate of reaction was directly proportional to the quantity of reactive aggregate remaining at a given time was found to be unsuccessful. The model was developed to take account of the alkali content of the cement and the alkalinity of the pore solution, and enabled the time required before cracking of the specimen was induced (T_c) to be predicted using the equation;

$$Tc = \frac{-\ln[\exp(-1.5K_2A^5) - 0.004/VR]}{K_2A^5}$$

and that the expansion of the specimen as a function of time could be predicted by;

$$\text{Expansion} = K_4\ \{VR[\exp(1.5K_2A^5) - \exp(-K_2A^{K_3}t)] - K_5\}$$

where the constants K_2 to K_5 were determined for Beltane opal graded to 150 to 300μm in size and stored at 20°C.

K_2 1 x 10^6 K_3 5 K_4 0.75 K_5 0.004

VR Volume concentration of Beltane opal in mortar.

A Alkali concentration of the pore solution when reaction is complete (calculation for A shown in reference 78).

The permeability and microstructure of plain and blended cements have been studied using a variety of techniques from microscopic study(66) to physical determinations of the pore size distribution (124,125) and rate of ionic diffusion (93-96). It has been established that the permeability of cement pastes increases exponentially with increasing water cement ratio and is reduced by progressing hydration and age. Although the higher water cement ratios increase the total porosity of the cement pastes they have little effect on the volume of pores less than 132nm in size. Therefore, the permeability of cement pastes is more closely related to the volume of the larger pores (greater than 132nm) rather than the total porosity(126). The permeability of cement pastes has been found to decrease when slag or pfa are blended with the cement.

Marsh et al(125) examined the influence of pfa on the pore structure of cement pastes using MIP and helium pynicametry. By comparison of the pore size distributions obtained from each method they determined that the pore structure of pfa blended cements consisted of relatively large but discontinuous thin walled pores. It was noted that the latter method provided a smaller value of porosity than the former. This suggested that the mercury was disrupting the pore structure and breaking through some of the thin pore walls. From depletion of calcium hydroxide measured at various curing temperatures it was observed that the reduced permeability of the ash blended specimens correlated to the extent of the pozzolanic reaction. From this it was concluded that the pfa present in the cement was blocking the capillary pores with pozzolanic reaction products. This mechanism was also observed by other workers(126,127) and a similar mechanism was noted by Bakker(22) for slag cements.

Several groups of workers(93-96,128,129) have used various techniques to measure the diffusion of ions through mature cement pastes and concretes. From these studies it was noted that cements blended with pfa or slag were able to reduce the rate at which these ions were able to diffuse through the matrix. This reduction in rate could not be attributed solely to the changes in the pore size distribution and other mechanisms were involved(126). Uchikawa(126) attributed these addition control mechanisms to the composition, structure and interfacial characteristics of the cement hydrates. Uchikawa noted that the mobility of the anions were reduced to a greater extent than the codiffused cation when passed through blended cements, and suggested that this was due to the higher Zeta potential of pozzolanic cement. In contrast Takagi et al(130) attributed the reduced ion mobility in blended cements to the positive electrical surface charge of the cement hydrate. This was regarded as a mechanism for allowing anions to pass easily but repelling the cations and it was suggested that blended cements achieved most of their effect by electrical repulsion . Despite extensive studies on the mobility of various ions in cement pastes and concretes, little work has been reported on the diffusion of hydroxyl ions. However, the steady state diffusion techniques developed by Kondo et al(93) and successfully used by other workers(87,94-96,129) provided a method by which the rate of alkali ion transport through blended cements could be compared to the observed expansion control measured for specimens produced using various cement blend combinations.

3.3 Experimental Procedure

The data generated within this chapter was obtained from expansion measurements made on mortar specimens stored under solutions of various alkali concentrations, steady state diffusion measurements and mercury intrusion porosimetry. The expansion specimens were based on a mix design which was known to be unreactive during its curing period. The mortar was produced using the low alkali cement A (0.225% equivalent soda) with an aggregate cement ratio of 2.75 and water cement ratio of 0.55. The aggregate consisted of 5mm down Cheddar limestone which alone proved to be inert under all the experimental alkaline solutions. Beltane opal graded in size between 300 and 150μm was used at the proportion of 12 grams per 100 grams of aggregate to induce alkali sensitive expansion. The Cheddar limestone was also graded to allow the Beltane opal fraction to be included without changing the overall particle size distribution of the fine aggregate unduly. An example of the mix design calculation is shown in Appendix 3.

The constituents of each mortar specimen were batched and mixed as described in 2.2.1. The mortar specimens were then cast in machined steel moulds in groups of six (see Figs 1.11 and 1.12 in Appendix 1), each prism measuring 170 x 40 x 10mm. After 24 hours curing at 20°C, the specimens were demoulded, individually marked, wrapped in plastic film and cured at 20°C for 56 days. When the mortar prisms were fully mature they were removed and two Demec spots were stuck onto one of the larger surfaces at 6 inch centres. The epoxy resin adhesive was allowed 24 hours to cure before the specimen was completely submerged (Fig 1.10) in one of a range of alkaline solutions. The specimens were allowed to equilibrate in the solution for 7 days before the first measurement between the Demec spot centres was made using a dial gauge capable of recording changes of 0·0001 inches (as shown in figure 1.12). The hydroxyl ion concentrations of the alkaline solutions were also measured and the solutions changed periodically.

Two experimental series of mortar prisms were produced. The first series of prisms used a plain cement mortar, which was subjected to a range of alkaline solutions produced using sodium and potassium hydroxides representing concentrations equivalent to pH13.0, 13.30, 13.45, 13.60, 13.75 and 13.90, at both 20°C and 38°C.

The second series of specimens were produced using a range of blended cement mortars, which were stored at 20°C under sodium hydroxide solutions of pH 13.30, 13.45, 13.60, 13.75 and 13.90. The blended cements were produced by substituting cement A by 20 and 40% of pulverized fuel ashes 2, 3, 4 and 5 in turn or by 40 and 60% ground blastfurnace slags 1, 2 and 3 in turn.

Equivalent specimens to those used in the expansion work were produced for pore size distribution determination. The measurements were made on specimens which had been cured for 56 days, then oven dried and tested as described in section 2.2.5. These specimens did not contain any reactive aggregates.

In addition to the mortar specimens produced for the expansion and pore size distribution measurements. A series of pfa blended cement pastes were made and used to compare the effect of each pfa on the rate at which alkali ions were able to diffuse through the cement paste. The paste specimens were made using cement A, 20% of which was in turn partially replaced by pfa's, 2, 3, 4 and 5. A water to cement and pfa ratio of 0.5 was used and the specimens were produced and cured as described in section 2.2.6.

The data recorded from the expansion study has been presented graphically as a function of time in Figures 3.2 to 3.25 of Appendix 3. Analysis of this data used to provide information on the time to initial expansion and expansion rate is given in Tables 3.4 to 3.23 with graphical interpretation shown in Figures 3.26 to 3.35.

The pore size distributions obtained for each material are shown in Appendix 3 in Figures 3.36 to 3.41 and the data collected from the steady state diffusion specimens for hydroxyl ions in Tables 3.24 to 3.28 and for sodium ions in Tables 3.29 to 3.33.

The results obtained have been analysed and discussed using the terms shown below. The calculations used in the analysis of the expansion data are also included for reference purposes.

Definitions

% Expansion

$$\frac{\text{Increase in recorded prism length}}{\text{Original prism length (as measured after 7 days submersion)}} \times 100\%$$

Time to initial expansion (To)

To = Age (hours) at which specimen attains an expansion of 0.03%.

Ultimate expansion

% expansion recorded at the end of the experimental period.

Calculations

Expansion time equation (Tables 3.4 to 3.18)

The calculated relationship between the specimen's expansion (%) and time during the steady state expansion period. Designed to show the change from a linear to parabolic function with increasing alkali concentration. Also used to calculate the expansion after 2688 hours.

To Mean Value (Tables 3.19 to 3.23)

For each cement blend

$$\text{To} = \frac{\text{Sum of To (hours) for each solution concentration}}{\text{Number of solutions}}$$

Effective diffusion coefficient (Tables 3.24 to 3.33)

Derived from Fick's first law (89)

$$D = \frac{\text{GRADIENT} \times V \times l}{A.\ \Delta C}$$

where

D	effective diffusion coefficient (cm^2S^{-1})
GRADIENT	Gradient of rectilinear plot of ion concentration increase on the low concentration side of the cell as a function of time
V	Volume of the low concentration side of the cell (cm^3)
l	Thickness of disc (cm)
A	Cross sectional area of disc (cm^2)
ΔC	Concentration difference across the cell (M)

To factor (Tables 3.20 to 3.23)

A comparison of reaction initiation times.

For each solution concentration

$$To = \frac{\text{To (hours) for blended cement}}{\text{To (hours) for plain cement}}$$

Permeability factor Eo (Tables 3.20 to 3.23)

A comparison of reaction induced expansion

For each solution concentration

Eo =

$$\frac{\text{Expansion (\%) @ 2688 hours}}{2688 - To}^{\text{blended}} + \frac{\text{Expansion (\%) @ 2688 hours}}{2688 - To}^{\text{plain}}$$

3.4 Results and Discussion

The data collected for the plain cement mortar prisms was rather limited due to the rapidity of expansion and the considerable change in specimen length, which exceeded the range of the measuring instrument. These prisms made using plain cement mortar were unfortunately unable to be remade due to the limited quantity of Beltane opal available. However, the data that was obtained is presented in Figures 3.2 to 3.5 of Appendix 3. The unbroken lines on these figures represent the actual recorded expansions, while the broken lines have been added to enable the time to initial expansion (To) to be estimated.

During the experimental time period expansion was induced in all specimens subjected to solution concentrations of pH 13.30 or greater. The time required to induce the initial expansion (To) into the specimens increased as the concentration of the solution was reduced. The relationship between the To and concentration of the solution appeared to be linear, as shown in Figures 3.26 and 3.27. Although the time was estimated for this series of specimens a strong correlation was observed and a similar correlation was recorded for the more accurately measured specimens of the second series. This trend was apparent for specimens stored under alkali solutions made with each hydroxyl type at both storage temperatures.

The rate that each specimen expanded was also influenced by the concentration of the curing solution. The rapidity of expansion increased with concentration upto a maximum rate of pH 13.75, this appeared to be a pessimum concentration. Specimens stored at 20°C under sodium hydroxide, as shown in Figure 3.2 and Table 3.4 demonstrated that at the lowest solution concentration (pH 13.30) a linear relationship between time and expansion existed. However, this relationship became increasingly parabolic as the concentration of the curing solution increased. The reasons for the change in this relationship are difficult to specify exactly, solely from the expansion measurements. However, the ASR is a solid/liquid reaction which in this experiment requires the alkali ions from the external solution to travel through the mortar matrix to the reaction sites on the surface of the silica particles.

This process might then be expected to be diffusion controlled, with the primary driving force being provided by the concentration difference between the external solution and the internal pore solution. In a system such as the specimens were subjected to the expansion measured as a function of time would be expected to correspond to a diffusion controlled reaction and thus produce a parabolic curve. That this does not happen for the specimens subjected to the lower concentrations may have been explained by Shu and Fen(101), who reported that the disintigration of the reactive aggregate continually exposed new reaction surfaces so countering the effects of the longer diffusion paths. This effect was noted in specimens made with various aggregates subjected to various temperatures whilst stored in a 10% potassium hydroxide solution.

However, if their observations of a linear time/expansion relationship were made under such experimental conditions, i.e in a potassium hydroxide solution of pH 14.25 then this would appear to contradict the findings of this study. In that only much lower concentrations produced a linear relationship. However, inspection of the expansion/time results shown for the specimens containing opal and cured at 20°C, Figure 1(a) in reference 101 would appear to have a parabolic relationship rather than the interpreted linear function. The change therefore from this linear relationship to the parabolic with increasing alkali concentration is probably attributable to reaction controlled kinetics. The aggregate appears to react and disintegrate at a rate depending on the supply of alkali ions. Below pH 13.60 the reaction proceeds steadily and produces a linear expansion. Above pH 13.60 the supply of ions appears to outstrip the speed of the aggregate reaction so the expansion rate reaches a pessimum level. The parabolic function observed for the higher concentration solutions may also be characterised by the progressive exhaustion of the silica present in the specimen, and is probably further complicated by the specimens macrocracks which result in an inefficient transfer of ASR stresses into length change.

The second series of specimens utilized blended cement mortar prisms stored under sodium hydroxide solutions at 20°C ranging in concentration from pH 13.30 to 13.90. This technique proved to be particularly effective for measuring the ability of cement replacements to control expansion due to ASR. It had the advantages of allowing time for the pozzolanic replacement material to hydrate before the reaction was induced in the specimens. Secondly, the simulated pore solution allowed different replacement materials and various replacement proportions to be examined at known pore solution concentrations thus overcoming difficulties of variable alkali dilution.

The expansions measured as functions of time and curing solution concentration for this series of specimens are shown in Figures 3.6 to 3.25 in Appendix 3. Each blended cement combination provided some beneficial control over the expansion process. The relative effectiveness of each blended cement was largely determined by the type of replacement material used, its replacement proportion and the concentration of the curing solution. However, within these general criteria each material's own individual characteristics also produced some noticeable variation in performance.

The ash blended specimens at both replacement levels were able to delay the To, compared with the plain cement mortars. The relationships between To and the curing solution concentration for each of the ash blended specimens have been extracted from the data and are shown in Figures 3.28 and 3.29 and tabulated in Tables 3.5 to 3.12. As observed for the plain cement mortars the To for each pfa blend decreased as the solution concentration increased. At 20% ash replacement, large reductions in the time to initial expansion were apparent with each concentration increase upto pH 13.60. Further concentration increase above pH 13.60 produced smaller reductions in the To. When 40% ash was included in the mortar prisms the To at each concentration level was generally greater than that achieved by the lower replacement proportion. Although there was an increasingly progressive reduction in the effect of the concentration on the To above pH 13.60, it was only observed for the high alkali ashes 2 and 3. The low alkali ashes 4 and 5, in contrast appeared to be more effective at the lower concentrations and provided a reasonably linear reduction in the To as the concentration was increased above pH 13.45.

The To for each pfa at both levels of replacement could also be correlated with their subsequent rate of expansion and ultimate expansion. Specimens with a short To produced rapid expansion and produced the greatest ultimate expansions. Conversely, specimens which required longer times to initiate expansion generally had slower expansion rates and smaller ultimate expansions. It was also evident, as for the plain cement mortars that the general rate of expansion for each pfa blend increased with the concentration of the solution up to a maximum of pH 13.75. The specimens containing a higher proportion of pfa were better able to control the rate of expansion and limit the ultimate expansion. It was observed that the relationship between time and expansion of the pfa blended specimens became increasingly parabolic as the solution concentration increased. These relationships have been calculated and are described for each pfa blend in Tables 3.5 to 3.12. The equations were also used to calculate the expansion of specimens after 2688 hours. Fig 3.32

From the data recorded it was difficult to precisely rank each ash by its effectiveness in controlling expansion. The relative performance of each ash varied between replacement proportions and across the solution concentration range. However, generally pfa 3 proved to be the least effective ash particularly at 20% inclusion across the range of curing solutions. Pfa's 4 and 5 performed well at both replacement levels and across most of the concentration range.

The blastfurnace slag blended mortars were also able to exert considerable control over expansion due to ASR. The degree of control was significantly influenced by the slag proportion of the mortar, larger replacements provided extremely good control over expansion. The expansions measured as a function of time for each slag blended specimen are shown in Figures 3.16 to 3.25. As with previous specimens the expansion rates increased with the concentration of the solution up to a maximum at pH 13.90, but maximum ultimate expansion was observed at pH 13.75 for both slag replacement levels. The mortar specimens containing 40% slag typically produced ultimate expansions similar to those achieved by the addition of 20% pfa, but the rates of expansion appeared to be slower and the times to initial expansion were considerably longer for the slags particularly at the lower levels of concentration. When

60% slag was substituted little or no expansion was recorded over the 280 day experimental period for prisms stored in solutions of concentrations upto pH 13.60. Further increases in concentration resulted in limited increases in the expansion rate and ultimate expansion.

The slag blended mortars, as observed for the other specimens had reduced To's as the curing solution concentration increased, this is shown in Tables 3.13 to 3.18. For prisms containing slag each concentration increase resulted in an almost proportional reduction in the To. However, when 60% of the cement was replaced by each slag considerably longer times to initial expansion were measured and the increase in solution concentration had a much smaller effect in reducing the time required. This is shown by the comparatively shallow gradients of the lines in Figure 3.31 compared to Figure 3.30.

As the technique used was able to compare the ability of each cement to resist ASR expansion free from any alkali dilution effects created by the inclusion of various replacement materials, the control exerted by each blended cement was attributed to its physical properties i.e. reducing the ingress of alkali ions and water through the matrix. Previous workers(22,41) have reported that blended cements can significantly reduce both the mobility of ions and permeability to water. In this work, attempts were made to correlate the observed control over expansion to their reduced permeability. However, this correlation was only of limited success. The pore size distribution measured by MIP for the blended cement pastes demonstrated reductions in the volume of the larger pores and an increase in the total porosity. These findings were in agreement with those of Uchikawa(126). The volume reduction of pores ranging from 150 to 1000 nm generally correlated quite well with the degree of control over expansion exerted by each cement blend. The lower inclusion level of pfa appeared to have little effect on the distribution of the pore sizes from that measured for the plain cement. When the same pfa's were included at 40% modest reductions in the volume of the larger pores (150 to 1000 nm) were measured. The pore size distribution for each pfa are shown in Figures 3.36 and 3.37, although the effect is more clearly demonstrated by the mean distributions plotted in Figure 3.40. The slag blended cements produced significant reductions in the volume of the larger pores, the larger additions of slag generally provided a greater reduction. The pore size distributions of each slag are shown in Figures 3.38 and 3.39, with the calculated mean for each replacement level shown in Figure 3.41.

An attempt was made to relate the permeability of the blended cements directly to the control over expansion by measuring the steady state diffusion rates of ions through blended cement pastes. Although these specimens were able to demonstrate that the inclusion of 20% pfa with the cement was capable of reducing the rate at which both hydroxyl and sodium ions were able to diffuse through cement pastes, as shown in Tables 3.24 to 3.33 and summarized in Table 3.1, it proved difficult to directly correlate the diffusion coefficients obtained for each pfa blend to their observed control over expansion when subjected to alkaline solutions. A comparison of the relative rankings obtained by each method is shown in Table 3.2.

Table 3.1 Effective diffusion coefficients of OH and Na ions.

Cement Blend	Diffusion coefficients of OH ions at 38°C cm^2/sec^{-1} x E8	Diffusion coefficients of Na ions at 38°C cm^2/sec^{-1} x E8
Cement A	8.70	8.25
A c/w 20% PFA 2	2.38	2.45
A c/w 20% PFA 3	0.76	1.30
A c/w 20% PFA 4	1.32	1.38
A c/w 20% PFA 5	2.30	2.64

Table 3.2 Comparison of measured ion mobility to observed expansion control

*

Ability of Blended Cements of Reduce Mobility of OH ions	Relative Ranking	Ability to Control ASR Expansion (Ave To)
A c/w 20% PFA 3	Best	A c/w 20% PFA 5
A c/w 20% PFA 4		A c/w 20% PFA 2
A c/w 20% PFA 5		A c/w 20% PFA 4
A c/w 20% PFA 2		A c/w 20% PFA 3
Cement A	Worst	Cement A

The apparent differences between the pfa's relative ranking as determined by each method of measurement may be due to attempting to compare a steady state constant diffusion rate to an indirect diffusion rate, based on the expansion of specimens. The relatively crude method of measuring permeability by expansion was subject to variations due to changing reaction factors which were probably sufficient to overcome and confuse relatively small differences in the diffusion rates measured for each ash. In retrospect, such a limited study of permeability may have been better served by the comparison of a single pfa and slag at each replacement level to the mean control over expansion observed by each cement blend. However, that blended cements were able to achieve some of their effect by reduced permeability was confirmed. The control over expansion and thus the permeability of the specimens appeared to be primarily determined by the type of replacement material and its replacement proportion. The effectiveness of each cement blend in controlling ASR expansion by reduced ionic mobility/permeability was estimated using the mean To values obtained for each cement blend as shown in Tables 3.19 to 3.23 and Figures 3.34 and 3.35 in Appendix 3. Based on these figures and the assumption that ASR is a two phase mechanism consisting of a reaction phase and an expansion phase and that the initial expansion of specimens signified the start of the expansive phase. Then the To would correspond to the time required for the reaction phase. Therefore, if all the experimental conditions were constant for each specimen the only variables which would influence the time required to complete the reaction would be those which influence the rate of alkali supply. i.e. the alkali concentration of the solution and each specimens' microstructure. Using these assumptions the following observations were made.

The apparent spacing of the "best fit" straight lines on Figures 3.34 and 3.35 indicated the relative ability of each blend type to resist the passage of alkali ions. Strong linear relationships between the change in the rate of reaction (To duration) and the concentration of the solution existed for each blended cement range of specimens. The reaction (To) took longer to complete in specimens that had a limited rate of alkali ion supply; this limitation could be achieved either by the curing solution having a low alkali concentration or by the material resisting the passage of alkali ions. The average times required to complete the reaction are summarized in the Table 3.3 below. From these results it appears that blended cement specimens could reduce the passage of alkali ions by up to 15 times when compared to the plain cement. The considerably superior performance of the large slag replacement specimens over the other cement blends also produced smaller changes in the rate of reaction (shown by the decrease in To) as a function of the solution concentration. From the gradient of the line passing through the range of To values the rate of reaction was increased by one unit for every unit increase in solution concentration. In comparison, all the other blends of cement including the plain cement mortar shared a common change in the rate of reaction. The reaction rate approximated to an increase of two units per unit increase in the solution concentration. This suggested that the rate of reaction had a second order dependence on the hydroxyl concentration of the pore solution in plain cements and those containing up to 40% pfa or slag. The rate of reaction for cement blends containing 60% slag had a first order dependence on the hydroxyl ion concentration. A summary of the gradients obtained for each material are shown in the table below.

Table 3.3 Summary of the relationships between expansion and pore solution alkalinity

Cement Blend	Ave To Factor	To Us pH gradient	Ave permeability factor
Plain	-	1.90	-
20% PFA	3.75	1.90	4.33
40% PFA	6.75	1.90	7.31
40% Slag	5.11	2.08	3.21
60% Slag	15.76	0.92	9.05

If it is assumed that the time to initial expansion provided an indication of the alkali mobility, then the rate at which the specimens subsequently expand after the To value is attained should provide some indication of the alkali silica gel's water imbibition rate. From the expansion data collected in Tables 3.19 to 3.23 it was apparent that each blended cement combination was capable of reducing the expansion rate, hence the rate at which the gel was able to imbibe water. The range of permeability reduction achieved by the blended cements varied with the type of replacement material used and the proportion of cement replaced. There was also some evidence to indicate that the rate of water imbibition increased with the concentration of the solution. This suggested that the water imbibition process was controlled jointly by the permeability of the material (shown by the large differences in expansion rates across the solution concentration range between various replacement materials) and the progression of the reaction processes breaking down the rigid siloxane framework of the gel allowing it to swell by the imbibition of greater quantities of water. From the expansive specimens measured the expansion rate of blended cement samples was reduced by upto 9 times compared to that of plain cement mortars.

It was apparent that expansion due to ASR could eventually be induced in blended cement mortar specimens by submersion in solutions of extremely low concentration. However, it should be noted that experiment involved the use of a highly reactive aggregate and a large volume of simulated pore solutions In practice, it would be unlikely that pore solution concentrations as low as pH 13.30 (200 millimoles of hydroxyl ions per litre) would present any threat of expansive ASR. In real mortars and concretes the quantity of alkali ions in the pore solution would be reasonably fixed. Therefore, if any reaction did take place and some gel was formed, the alkali ions would be consumed and not continually replaced as was the case in the experimental pore solution. The resulting expansion, if any, would then be determined by the quantity of ions available in the pore solution.

3.5 Conclusions

1. The addition of pfa and slag to cement mortars delayed the time to initial expansion and reduced the rate at which the specimen subsequently expanded.

2. The degree of control exerted over expansion was dependent on the type of replacement material and the proportion included.

3. The rate of reaction (as determined by To) appeared to have a second order dependence on the hydroxyl ion concentration for plain cements and those containing upto 40% pfa or gbfs, suggesting a common rate controlling process.

4. The rate of reaction in cement blends which included 60% slag appeared to have a first order dependence on the hydroxyl ion concentration, suggesting a different rate controlling process.

5. The relationship between the expansion (%) and time for plain cements are those containing upto 40% pfa or gbfs appeared to be linear at low concentrations (pH 13.30), but became increasingly more parabolic with increased concentration.

6. It was observed that reaction could be induced at relatively low concentrations if unlimited quantities of alkali was available.

7. It was difficult to directly correlate the control over expansion in the mortar bars to steady state diffusion coefficients obtained for blended cements containing 20% pfa.

8. Curing mortar prisms in alkali solutions proved to be an effective technique for rapid inducement of ASR and provided a simple method to determine the effect of various pore solution concentrations on ASR.

CHAPTER 4

The effect of Cement Alkalis on the Pore Solution Composition

4.1 Introduction

The work in the previous chapter demonstrated that blended cement mortars could control ASR expansion partly by mechanisms associated with their reduced permeability. The objective of this and the following two chapters was to examine the effect that various Portland cements and blended cement combinations had on the pore solution composition. The composition changes produced by the various blends have been used to establish the factors which influence the effectiveness of replacement materials to control ASR expansion by their alkali dilution properties.

This chapter was primarily concerned with the alkalis present in cement and their influence on the alkalinity and composition of the pore solution. It is currently recommended that the limitation of alkalis within concrete provides a reasonable precaution against ASR. The significance of the cement alkali content and the effect of the total alkali content of concrete on the pore solution alkalinity have been examined. The relative effectiveness of each method was assessed.

4.2 Previous Work

The study of the liquid phase of hydrating cements has been of interest for many years. Early investigations by Roller(24,25) and Kalousek et al(26) in the 1930's and 1940's used simple filtration devices to obtain liquid samples and were able to establish the changes in chemical composition of the solution during the initial stages of cement hydration. This technique was latter developed by Lawrence(27) and Roberts(28) who retarded the set of cement slurrys by continuous agitation, so extending the measurement period. Attempts to measure a pore solution composition which was more representative of normally cured cement pastes were made by a number of different techniques. These methods involved the use of solvents(29-32) to displace the aqueous phase and the use of embedded electrodes to measure the pore solution ion concentrations(33,34). Longuet et al(35) in 1973 developed the first effective apparatus for expressing the pore solutions from mature cement paste specimens. Several groups of workers(36-39) have since used similar devices to successfully express pore fluids from mature cement pastes.

Longuet(104) used the expression device to measure the pore solution composition of cement pastes up to two years old. He reported compositions similar to those described by the earliest workers(24-26). That is, on addition of the mixing water the liquid phase became rapidly enriched with increasing amounts of sodium, potassium, hydroxyl, calcium and sulphate ions. After several days, the pore solution consisted essentially of sodium and potassium hydroxides, with only trace quantities of calcium, sulphate and some other ions present. The sodium, potassium and hydroxyl ion concentrations increased up to a maximum between 7 and 28 days, after which time they were maintained or decreased slightly(39,104)

The relationship between the alkali content of the cement and the pore solution alkalinity has been studied by several workers(37,38,104-106,108) Table 4.1 and Figures 4.1 and 4.2 in Appendix 4 compare these workers findings, which have been adjusted to an approximately common water content of 0.5. A highly significant correlation (correlation coefficient of approximately 0.9) between the alkali content of the cement used and the hydroxyl ion concentration of the pore solution was observed over a wide range of equivalent soda contents.

Less work has been reported on the expression of pore solution from cement mortars and concretes. Barneyback(39) monitored the changes in pore solution chemistry of high alkali content cement mortar specimens as they progressed through the ASR process. More recently Kollek et al(105) published work which detailed the hydroxyl ion concentrations obtained from the pore solutions expressed from plain and blended cement mortars. The mortar specimens were produced using three Portland cements, a range of replacement materials and a reactive aggregate. The pore solution hydroxyl ion concentrations were related to expansion bar measurements. No work specifically related to the alkali content of the cement and its influence on the pore solution alkalinity of concrete or the effect of total alkali content of concrete on their pore solution composition was found in the literature, although Nixon and Gaze(40) had studied the effect of various total alkali content concretes by use of expansive concrete prisms.

The work in this chapter has attempted to address these gaps in knowledge and attention is drawn to the significance of the two methods of alkali limitation currently being recommended in standards(61).

4.3 Experimental Procedure

The experimental work in this chapter was undertaken with three series of specimens. The first series of specimens was designed to confirm the relationship between the alkali content of the cement and the alkalinity of the resulting pore solution. This series of specimens also served to provide reference data, against which subsequent pore solution measurements could be compared. Cements A,B,C and D which had equivalent soda contents of 0.225, 0.67, 0.86 and 0.94% respectively were used to produce cement paste specimens at a water cement ratio of 0.5. These specimens were batched and mixed as described in 2.2.1 and cured in sealed containers at 20°C for 7, 28, 84 and 365 days.

The second series, were equivalent cement mortars made with Cheddar limestone aggregate introduced at a ratio of 2:1 by weight of cement. These specimens were designed to establish the effect that a non-reactive aggregate addition would have on the pore solution of the previously referenced cement pastes. The specimens were produced and cured under the same regime as those described for the first series.

The objective of the third experimental series of specimens was to produce concretes of given total alkali content expressed as kilograms of equivalent soda per cubic metre using cements of various alkali content, to assess the effectiveness of limiting the total alkali content of concrete. This method is currently suggested as being a more flexible alternative to the use of low alkali cement as a precaution against ASR(61). Concrete specimens were produced using cements A,B,C and D at a water cement ratio of 0.5 and an aggregate fines to coarse ratio of 40:60. By varying the proportion of each cement present in the mix, total alkali contents of 2,3,4 and 5Kg of equivalent soda per cubic metre of concrete were produced. The remaining constituents were then designed using the Department of the Environment method(51). The concrete was produced as previously described in 2.2.1 using saturated, surface dried coarse aggregate and cured at 20°C for 28 days.

The pore fluid expressed from each specimen was analysed for hydroxyl, potassium and sodium ion concentrations using the methods described in Section 2.2.3. The free water content of each specimen was a relative measure (see Section 2.2.4) estimated by heating to constant weight at 105°C. The experimental results obtained are located in Appendix 4 and are presented in Tables 4.2 to 4.6 with graphical interpretations shown in Figures 4.3 to 4.20. The data presented in Tables 4.1 to 4.6 was analysed using the calculations shown below and are included here for reference.

<u>pH (Tables 4.1 - 4.3, 4.5)</u>

$$pH = 14 + \log_{10} [OH^-]$$

<u>Corrected Concentration (Tables 4.1 - 4.3)</u>

$$\text{Measured concentration} \times \frac{\text{free water content}}{\text{original water content}} \quad \text{(mmols/l)}$$

<u>Quantity of ions in solution (Tables 4.1 - 4.3, 4.5)</u>

Measured ionic concentration x free water content (mmols/g cement)

<u>Ion difference on the addition of aggregate (%) (Table 4.4)</u>

ΔQ= Difference in quantity of K or Na ions between paste and mortar

$$\frac{\Delta Q}{\text{total ion quantity available from the cement}} \times 100\% \quad \text{(mmols/g cement)}$$

4.4 Results and Discussion

4.4.1 Cement Pastes and Mortars

The data obtained from the analysis of the pore solutions expressed from the cement paste and mortar specimens are recorded in Tables 4.2 and 4.3. As expected from the findings of previous workers, the pore solution ion concentrations increased with the alkali content of the cement used to produce them. The hydroxyl ion concentration of each specimen also varied as a function of time, the changes measured being shown graphically in Figures 4.3 and 4.4 for cement pastes and mortars respectively.

The cement paste specimens were ranked by the alkali content of the cement, this relative ranking was maintained throughout the duration of the experiment. The pore solution hydroxyl ion concentration of each cement paste increased up to a maximum at 84 days, this concentration was then maintained or reduced slightly during the remainder of the experimental period. The mortar mixes demonstrated similar trends in ranking and concentration change as a function of time. However, the addition of aggregate to the cements reduced the general hydroxyl ion concentration of the pore solution compared to its equivalent cement paste specimen and this became increasingly apparent during the later part of the period. The actual concentration difference between the mortar and paste specimens increased with the alkali content of the cement.

The specimens were cured in airtight containers which resulted in a closed hydration system. That is, the included water was not allowed to escape or be added to from external sources. Therefore, in such a system the changes in the ionic concentration may be attributed to three mechanisms during the cements hydration process(106).

a) The dissolution of alkali ions from the hydrating cement into the pore solution.

b) Ion removal from solution by incorporation into solid hydration structures or reaction products.

c) The reduction of the free water content due to continued cement hydration.

Then at any particular time the concentration of ions in the pore solution is the resultant of these interrelated and continually changing mechanisms. The changes in concentration recorded for the paste and mortar specimens that may be attributed to the net movement of hydroxyl ions into or out of the pore solution may be determined if the concentration is corrected to take account of the reduction in free water accompanying the cement hydration process. This method is similar to Diamond's(106) water concentration factor, which was defined as the corrected ion concentration of the pore solution had the bound water removed by cement hydration been replaced by an equal quantity of water from an external source. The calculation used to correct the data in this work is shown in Section 4.3.

The corrected concentration shown in Tables 4.2 and 4.3 demonstrated that the net movement of hydroxyl ions in and out of the pore solution corresponded to the trends of concentration change for each cement paste and mortar specimens. However, the ion movements were relatively small compared to the changes in concentration measured which indicated that much of the change in concentration measured was attributable to the reducing free water content. The larger proportion of unbound water present in the mortar specimens resulted in a greater ion dilution effect which resulted in significantly reduced measured hydroxyl ion concentrations. However, even when the unbound water contents were corrected the mortars were able to still achieve some reduction of the ions in solution when compared to the equivalent paste specimens. It appears that the aggregate may absorb the balance of the hydroxyl ions. The quantity of ions absorbed may be connected with the alkali concentration of the pore solution, although insufficient data exists to form a more comprehensive hypothesis on this relationship. Collins and Bareham(107) have also found evidence that would suggest that aggregates may absorb some of the alkali ions present in the pore solution. They reported that expansive mortar bars made using porous aggregates were able to reduce the expansion due to ASR significantly. Further investigations into the influences that different proportions and types of aggregates have on the pore solution composition of cement mortars would be of interest.

The hydroxyl ion concentrations of the pore solutions when plotted as shown in Figure 4.2 compare favourably with those of previous workers (Table 4.1 and Figure 4.1). There is some degree of scatter although the points fall within a general envelope which suggested a linear relationship between the pore solution hydroxyl ion concentration and the cements' alkali content. The cause of this scatter may be due to either real differences in the alkali release characteristics of cements containing similar quantities of alkali or to variations in experimental technique. If various cements do have variable alkali release properties then doubts over the effectiveness of specifying low alkali cements (those below 0.6% Eq Na_2O) as a precaution against ASR in particularly severe environments would exist. In this work the experimental variation should at least have been reduced, however, a small degree of scatter was still apparent for the four cements used. The change in ion concentration of each cement as a function of time also appeared to be an individual characteristic, which would seem to indicate that there was some degree of variation in the proportion of alkali ions released by each cement into the pore solution. It was difficult to draw further conclusions on the extent of the variability of this alkali release from the data collected in this work.

The combined potassium and sodium ions present in the pore solution approximately balanced the hydroxyl ion content. The general ranking of concentration and quantity of these ions in solution were determined primarily by the relevant oxide content of the cement. The general trends of concentration and ion quantity change for the potassium and sodium ions were similar to those observed for the hydroxyl ions. These changes in ion concentration and quantity as a function of time are shown in Figures 4.11 to 4.14. It was apparent that the addition of aggregate had the effect of modifying the ions present in the pore solution and appeared to reduce the quantity of both potassium and sodium ions in solution. The actual quantity of ions removed tended to increase with potassium/sodium content of the cement used. The addition of aggregate to the cement appeared to have a greater influence on the potassium ions than the sodium ions in solution as shown in Table 4.4. The mortars removed more potassium ions both in terms of millimoles and proportion of the total ions present in the cement. This had the effect of reducing the potassium to sodium ratio for the mortar specimens, and appeared to reduce the large changes in this ratio observed for the paste specimens as shown in Figures 4.15 and 4.16.

4.4.2 Concretes

The third series of specimens was designed to produce concrete specimens of predetermined total alkali contents, using cements of various alkali content. The mixes utilized a fixed water to cement ratio, this combined with the considerable changes in the cement component required to achieve the total alkali contents of the concretes caused problems of variable consistencies and workabilities. Table 4.6 in Appendix 4 illustrates the quantity of each cement required to achieve the designed total alkali content of each concrete. As a consequence of this variability, pore solutions could not be expressed from concretes made from cements B,C and D at the 2 kilogram of equivalent soda per cubic metre of concrete, the specimens being "too dry".

The data recorded from the expressed pore solutions are shown in Table 4.5 with graphical interpretations shown in Figures 4.17 to 4.20 in Appendix 4. From Figure 4.17 it was evident that the hydroxyl ion concentration of the pore solution was primarily determined by the alkali content of the cement used to produce each range of total alkali contents. The distinct ranking of hydroxyl ion concentrations which increased with the cement alkali content was similar to that observed for the cement paste and mortar specimens of the earlier series. It was also apparent from Figure 4.17 that within those general rankings, the concentration of ions for each cement also increased with the total alkali content of the concrete. Cement A (0.225% equivalent soda) was the exception and did not significantly change in concentration at any total alkali content.

It was observed in Table 4.5 that the relative proportions of cement and aggregate present in the concrete appeared to influence the unbound water content. Concretes with low cement, hence high aggregate contents (Table 4.6) had larger free water proportions (Table 4.5). As the cement content of concrete increased so the influence of the aggregate became less significant, this was noticeable in the cases of cements A and D. This suggested that the aggregates may have released some water into the pore solution creating increased dilution of the alkali ions. The released water may be present due to the saturated surface drying process of the coarse aggregates. Each concrete made using cement A contained a considerable proportion of cement and therefore little aggregate. It was noted that these concretes demonstrated little change in the hydroxyl ion concentration of the pore solution as the total alkali content of the concrete was increased, as shown in Figure 4.17.

The quantity of hydroxyl ions released into solution by each cement, per gramme, was primarily a function of the alkali content of the cement, as shown in Table 4.5 and Figure 4.18. The actual quantity of ions appeared to decrease slightly as the total alkali content of each cement increased. This trend was thought to be misleading and attributable to the increasing aggregate component together with its larger proportion of unbound water confusing the calculation. When the quantity of ions released by each cement per cubic metre of concrete was calculated, as shown in Figure 4.19, then the quantity of ions released by each cement reduced as the total alkali content of the concrete was reduced. In Figure 4.20 it was observed that concretes made with cement A, an extremely low alkali cement, released considerably more hydroxyl ions into solution per cubic metre than concretes made with high alkali cements. However, this was due entirely to the vast cement content required to produce the given total alkali contents using cement A and should not be considered as a serious drawback to application of the limitation of the total concrete alkali content. The concretes produced were not intended to represent realistic concretes found in practice. Concretes produced using cements B,C and D which produced larger quantities of hydroxyl ions per gramme of cement could be balanced against a reduced quantity of cement required to produce the given total alkali content.

The concentrations of sodium and potassium ions present in the pore solution of the concretes followed a similar trend to that observed for the hydroxyl ions. The relative content of each ion within the cement appeared to be the primary influence which determined the general concentrations measured in the pore solution. The concentration of these ions increased with the total alkali content of the concrete.

The control of ASR by limitation of the total alkali content of concrete does provide a more flexible method of reducing the alkalinity of concrete. From the pore solutions expressed in this work, it was observed that both the concentration and quantity of alkali ions present in the pore solution of concrete could be reduced by limiting the total alkali content of the concrete. Cement of high alkalinity which produced a greater quantity of ions per gramme could be balanced against a lower cement content in a concrete, within limits. As seen with cement A, when excessive quantities of cement were used even the extremely low alkali content was unable to compensate for the quantity of ions produced. However, in practice it would be unlikely that concretes containing such considerable quantities of cement would ever be produced due to problems such as shrinkage. The mix design would more likely to be fixed by considerations of strength, cement content and the workability necessary to produce a durable and economic concrete.

From the data shown in Figures 4.19 and 4.20 it was observed that the total quantity of ions could be reduced by each cement if the total quantity of alkali present was limited. However, the actual alkali content of the cement used did result in some variation in the quantity of ions per cubic metre of concrete produced, and significant variations in the pore solution concentrations of concretes of equivalent total alkali content. These variable effects may be a result of the fixed water to cement ratio method chosen to design the concrete mixes. In retrospect, the influence of the cements' alkali content on the total alkali content of concrete might have been better demonstrated had a constant water content been employed instead. It is hypothesized that as the cement content is reduced, either to achieve a smaller total alkali content or because the cements inherent alkali content was high, then the effective water to cement ratio would increase so causing greater dilution of the ions released. The dilution effect being proportional to the cement content and hence indirectly to the alkali content of the cement, the large differences in concentrations between cements may have been reduced. However, the method actually employed does show the significance of the water content and the relative mix design on the alkali concentration and quantity of ions in the pore solution.

4.5 Conclusions

4.5.1 Cement Pastes and Mortars

1. The concentrations of hydroxyl ions in the pore solution of cement pastes and mortars were primarily governed by the alkali content of the cement used.

2. The addition of a nominally unreactive aggregate to the cement paste reduced the hydroxyl ion concentration of the pore solution, especially for the higher alkali cements.

3. The reduction appeared to be achieved mostly by the increased dilution effect created by the larger proportion of unbound water present in the mortars. However, there was some evidence to suggest that the aggregate was absorbing some ions from the solution.

4. The ionic concentrations measured for the cements were generally in accordance with the findings of other workers.

4.5.2 Concretes

1. The hydroxyl ion concentration of concrete pore solutions could be reduced by limiting the total quantity of alkali in the concrete.

2. At each level of total alkali per cubic metre of concrete the concentration of ions appeared to be influenced by the alkalinity of the cement used, although this was thought to be attributable to the method of mix design.

3. The relative quantities of aggregates and cement also influenced the concentration and quantity of ions in solution.

CHAPTER 5

Pore Solution Compositions of Blended Cements: Cement Variables

5.1 Introduction

The previous experimental chapter of this thesis examined alkalis in pore solution from various cements. This chapter continues this theme and examines the influence that partial substitution of cement by a hydraulic and a pozzolanic replacement material has on the pore solution.

It has been well documented that the addition of certain hydraulic or pozzolanic materials to concrete may provide a beneficial effect in reducing the damage due to ASR (see 1.4.4). Two of the most widely studied materials in this context are pulverized fuel ashes and ground blastfurnace slags. However, there is some evidence to suggest that these materials have variable degrees of effectiveness. Particular concern has been focussed on the significance and role played by the relatively large alkali contents found in some ashes and slags. The total alkali contents for British pfa's have been found to range from 0.75 to 4.6 % equivalent soda by mass(112), which is considerably in excess of that expected to be present in Portland cements. Blastfurnace slags may also possess a total alkali content equivalent to that expected for a high alkali cement.

The experimental specimens produced in this work were designed to study the effect that the partial substitution with a relatively high alkali ash and blastfurnace slag would have on the pore solution composition of a range of cements. The cements represented a considerable range of alkali contents to determine the influences, if any, this had on the pfa's/slag's ability to remove ions.

5.2 Previous Work

Many workers have assessed and compared the performance of various cement replacement materials with respect to ASR. Usually this has been achieved by monitoring the length change of expansive mortar bars, comparisons being based on their relative ability to suppress expansion. This technique has proved to be an effective means of appraising specific cement/replacement material/aggregate combinations, but it does not provide an explanation for the controlling mechanism. However, from this work it was generally thought that these replacement materials worked by diluting the cements alkalis. The dilution mechanism required that the replacement material contributed little or none of its considerable total alkalinity to the pore solution effectively acting as a low or zero alkali cement.

Several studies have examined the expressed pore solutions from mature blended cement specimens. The technique proved to be a useful method which enabled study of the alkali ion dilution/removal properties of the replacement materials and gave some indication of the chemical mechanisms occuring during hydration. Previous work(38,40,105) has shown that the addition of certain pozzolanic materials reduced the cements' pore solution hydroxide concentration. However, their effectiveness was found to be variable, some materials being able to reduce the alkali ions by an extent greater than could be accounted for solely by alkali dilution whilst others contributed alkalis to the pore solution.

Barneyback(39) demonstrated the influence of different types and replacement levels of various materials on the hydroxyl ion concentration of pore solutions. He produced specimens using single reference cement blended with silica fume, two types of commercial pozzolanas, a high alkali natural pozzolan (pumice) and an inert quartz sand. Each material appeared to reduce the alkali concentration roughly in proportion to the pozzolan present. However, the actual quantity of ions removed from the pore solution varied considerably with the type of pozzolan used. The extent of ion removal ranged from exceedingly high for the silica fume blends to negative (i.e. ion contribution) for the high alkali natural pozzolan.

Glasser and Marr(38) also produced specimens using a range of replacement materials and blended them with two cements. Each cement (0.905% and 0.505% equivalent soda) was replaced by 15% of each of two pfa's (3.6% and 1.2% equivalent soda), a slag (0.79% equivalent soda), a natural pozzolan (2.34% equivalent Na_2O) and two silica fumes (0.89% and 0.68% equivalent soda). The materials had similar alkali removal capacities to those reported by Barneyback. Glasser and Marr also noticed that the replacements performed differently depending on the alkalinity of the cement replaced and that of each pfa. Both pfa's and the slag proved to be more effective at reducing the pore solution pH of mortars made with the higher alkali cement than those made using the lower alkali cement. There also appeared to be some correlation between the alkali content of the pfa and its effectiveness in reducing the alkali ion concentrations. The higher alkali content pfa contributed ions, enriched the pore solution hydroxyl ion content of the mortars made with the low alkali content cement. This ash was also less effective in removing alkali ions from the high alkali cement mortar pore solutions. The lower alkali content pfa was able to reduce the pore solution alkalinity of both cement mortar types.

Diamond(106) working with two Danish fly ashes also observed that the ashes' alkali content influenced its ability to remove hydroxyl ions from solution. Diamond suggested that the difference in performance may also be a function of their physical fineness and/or due to the reactivity of the glass phase of the two ashes.

From the findings of these various studies, it has been suggested that alkali ions may be removed from the pore solution by the blended cements as a result of possibly two chemical reactions. In the first of these reactions, the finely divided amorphous siliceous content of the replacement material is thought to reduce the ASR potential by reacting more quickly with the alkaline hydroxide in the pore solution than the larger sand size reactive silica present in the aggregate(109). There is no deleterious expansion associated with this alkali pozzolana reaction. The quantity of hydroxyl ions available in solution for reaction is reduced to a level below the threshold of expansion(110). The second reaction was proposed by Glasser and Marr(38) and involves the relatively large quantities of silica present in some replacement materials altering the composition of the CSH which makes it capable of sorbing greater quantities of alkali ions. They originally suggested two possible mechanisms which would account for the CSH removing a greater quantity of alkalis. The first model requires the CSH itself to remove the alkali ions. Experimental data by Glasser and Marr and Bhatty and Greening(111) has demonstrated that the alkali ion removal properties improve as the calcium to silica ratio decreases, and is examined in greater detail in 6.2. The second mechanism which may not necessarily be completely separate from the first model also depends on a low C/S ratio CSH phase. Alkali ions are removed by precipitation of alkali containing compounds. Subsequent work by Glasser and Marr(20) has shown that the first model was thought more likely to be the primary mechanism of ion removal.

5.3 Experimental Procedure

The experimental data for this chapter was generated by the analysis of the expressed pore solutions from two series of blended cement paste specimens. The first series of specimens were produced using a single pulverized fuel ash, pfa 1, 3.40% equivalent soda to partially replace cements A, B, C and D, 0.225%, 0.67%, 0.86% and 0.94% equivalent soda respectively. The ash was substituted for cement at 0, 10, 20, 30 and 40% by weight of cement.

The second series of specimens were produced using a single blastfurnace slag, slag 3, 0.599% equivalent soda to partially replace cements A, B, C and D at 0, 40, 60 and 80% by weight of cement.

Triplicate specimens for each cement paste blend were produced using water to cement+replacement ratio of 0.45. The specimens were cured in sealed containers at 20°C for 28, 168 and 365 days. No adjustment to the water content was made to allow for reduced water demand created by the addition of the replacement materials.

The replacement levels selected for each series are representative of those used in practice and found to be effective in reducing expansion due to ASR. The expressed fluid from each specimen was analysed for hydroxyl, potassium and sodium ion concentration as described in 2.2.3.

The free water content of each specimen was also estimated using the method described in Section 2.2.4.

The recorded data has been presented in Appendix 5 in two parts. Firstly, those results and graphical interpretations for the pfa blended specimens are presented in Tables 5.1 to 5.6 and Figures 5.1 to 5.10. Secondly, the data and figures associated with specimens which were partially replaced using slag are presented in Table 5.7 to 5.16 and Figures 5.11 to 5.20. The data obtained has been analysed and discussed in terms similar to those described in Section 4.3, together with some additional terms which are defined below;

Equivalent OH dilution factor (DF) (Tables 5.1 - 5.3, 5.7 - 5.9)

This provides a theoretical measure of the replacement materials alkali ion dilution/removal effect. The factor demonstrates the effect in terms of the percentage reduction as compared to the original cement and is calculated;

$$DF = \left[1 - \frac{OH^- \text{ concentration of blended cement}}{OH^- \text{ concentration of plain cement}} \right] \times 100\%$$

Ions removed per gramme of replacement material (IR) (Tables 5.4 - 5.6)

This parameter was used to demonstrate the replacement materials ion removal capacity as a function of its inclusion proportion and was calculated;

$$IR = \frac{IB}{\text{Replacement proportion (\%)}}$$

where IB is the difference between the reduction in the quantity of ions measured for the plain and blended cement specimens over the experimental duration.

Estimate of ions contributed by slags (Table 5.15 and 5.16)

It was observed that some slag blend combinations increased the quantity of sodium and/or potassium ions in solution compared to those available solely from the cement proportion of the blend. The contribution of ions by the slag was estimated by subtracting the estimated ion quantity present from the cement content from the actual recorded ion quantity for the blended cement and was calculated;

$$(\text{Measured ion quantity (K or Na)})^{\text{blended cement}} - [\text{Estimated ion quantity*}]^{\text{plain cement}}$$

* Estimate based on portion of ions in plain cement and proportion of cement in the blended cement.

5.4 Results and Discussion

5.4.1 Pulverized Fuel Ash Replacement

The influence that the partial replacement of each cement by pfa 1 had on the hydroxyl ion concentration as a function of the replacement proportion and time are shown in Figures 5.1 to 5.6. To assist in the assessment of the effects that the pfa was having on each cement, a theoretically derived reference line was included for each cement. These lines, shown as broken lines on the figures, represent the hydroxyl ion concentration, calculated to exist had each cement been replaced by an inert material, which would dilute the cements' alkalis. For the purpose of calculation it was assumed that the material was effectively a zero alkali cement, and no allowance was made for changes in water binding capacity created by the replacement material. This effect is considered separately in the discussion. As such, the "alkali dilution" values are obtained by direct proportional reduction of the ion concentration measured for each neat cement paste specimen, at each age.

As observed in Chapter 4, the hydroxyl ion concentration of the pore solution was primarily determined by the alkali content of the cement. The influence of the pfa addition in reducing the pore solution concentrations apparent from the first measurement made at 28 days. The concentration reductions achieved by cements B, C and D increased with the proportion of pfa present in the mix, although at this age the concentrations were higher than expected, solely by alkali dilution. The quantity of hydroxyl ions in solution produced only very modest reductions as the proportion of pfa increased. From these observations, the reduction of the hydroxyl ion concentrations in the pore solution appear to be primarily achieved by the increased free water available by the ash's reduced capacity to fix water, diluting the hydroxyl ions in the pore solution. Although cement A has similar increases in the free water content, the addition of pfa enriched the pore solution with hydroxyl ions. The increase in the hydroxyl ions present in the pore solution tended to suggest that the pfa had released its water soluble alkali content. This release may have countered any useful reduction achieved by the reaction between the hydroxyl ions of the pore solution and the fine particles of amorphous silica present in the ash and/or any alkali dilution properties.

After 168 days, the pfa continued to contribute hydroxyl ions to the pore solution of cement A specimens, which caused both the concentration and quantity of ions in solution to be enriched above that of the plain paste. In contrast, cements B, C and D with pfa inclusions demonstrated reductions in both hydroxyl ion concentration and the quantity of ions in solution. At this age the hydroxyl ion concentration was reduced to a significant level below that expected solely by alkali dilution. This reduction in concentration corresponded with a significant removal of ions from the solution. The quantity of ions in solution correlated closely to the theoretical value calculated. The measured concentration and quantities of ions in solution were then approximately maintained or slightly reduced during the period up to 365 days. Although 365 days at 20°C is considered an insufficient time period for the pfa blended specimens to reach a steady state chemical balance , it was apparent that the majority of hydroxyl ions removed by the pfa were lost between 28 and 168 days.

From observations made on the relative differences between the hydroxyl ions recorded and those calculated to be in solution if the cement were diluted by an inert filler, the pfa's ion removal capacity appeared to vary with its inclusion proportion. Figures 5.3 to 5.6 demonstrate that when pfa was included in the proportions of 10 and 40%, proportionally small reductions in hydroxyl ions were achieved. Conversely, when the same pfa was included at 20 or 30%, relatively large reductions in hydroxyl ions were measured. The actual quantity of ions removed over the experimental period by each gramme of pfa at each replacement level has been calculated and is shown in Table 5.4. From this data it appeared that the ash became increasingly inefficient in removing alkalis as its replacement proportion increased. The reduced alkali sorptive capacity of the ash at the higher replacement proportions may be due to the release of significant quantities of alkali from the ash which has the effect of countering some of the pozzolanic removal capacity(38). In this work, the optimum level for pfa inclusion appeared to be that which provided a suitable balance between providing sufficient ash to alter the composition quantity of the CSH, but avoiding excessive additions which released large quantities of water soluble alkali.

The importance of the reduced water fixing tendency of the ash and its influence on the dilution effect of the ions in solution was apparent at all ages, as shown by the difference in equivalent dilution factors of the concentration and quantity of hydroxyl ions (Tables 5.1 to 5.3). The dilution factors represent the actual dilution of hydroxyl ions expressed as a percentage occurring at a particular time when compared to the control mix. In Appendix 8, 'A reply to the discussion of Hobbs and Gutteridge'(114); the hydroxyl ion concentrations were recalculated to take account of the ash's reduced water fixing capacity. It was found that when the reference lines were drawn to the redefined criteria (figure 4 of paper) the general trends described remained unchanged, but the pfa's alkali dilution properties did seem less marked and approximated to those described in the discussion of the quantity of hydroxyl ions in solution. Although no significant alkali contribution was recorded for pfa inclusions upto 30%, at 40% inclusion the hydroxyl ion concentration was increased above the reference line depicting expected values to be obtained by alkali dilution.

The influence of the pfa on the potassium ions in the pore solutions of the cements generally followed similar trends to those observed for the hydroxyl ions. Cements B, C and D were able to reduce the potassium ion concentration at the 28 day measurement approximately in proportion to the pfa content of the blend. The increased free water present in the ash blended specimens accounted for a significant proportion of the reduced concentration. However, the pfa's pozzolanic reaction over the experimental period also removed significant quantities of potassium ions from the solution. The actual quantity of ions removed increased with the proportion of pfa present, as shown in Table 5.6. When the data were recalculated in terms of ions removed per gram of pfa, its ion removal capability decreased as the proportion of pfa increased. Cement A, demonstrated significant increases in both the quantity of potassium ions and their concentration when pfa was blended. Although the quantity of ions in solution was reduced slightly as a function of time, (Table 5.6) a considerable surplus of potassium ions above those available solely from the plain cement were recorded. This excess of ions was presumed to originate from the ash proportion of the mix.

The concentration and quantity of sodium ions in the pore solutions of the cements were comparatively smaller than those of the potassium ions, which reflected the smaller sodium contents of the cements. The addition of pfa to the cements reduced both the concentration and quantity of ions in solution to levels approximately to those expected by alkali dilution.

The quantity of sodium ions in the pore solutions of the blended specimens appeared to increase slightly over the duration of the experiment. Although this involved the movement of relatively few ions it was a trend contrary to those observed for hydroxyl and potassium ions which were removed as a function of time. The extent of this movement is detailed in Table 5.6, and it compared to the potassium ion movements in Table 5.5. It appears that the potassium ions are removed preferentially to the sodium ions.

5.4.2 Blastfurnace Slag Replacement

Reductions in the pore solution hydroxyl ion concentrations of each cement were recorded when slag was present. For cements B, C and D these reductions approximated to those expected by alkali dilution, as shown in Figures 5.11, 5.13 and 5.15. When the slag was blended with cement A the reductions achieved were relatively large when compared to the effects of the pfa, but were not sufficient to provide a close correlation with the theoretical alkali dilution line.

The slag blended specimens had achieved virtually all of their ultimate concentration reduction by the time of the first measurement made at 28 days. In contrast to the action of pfa, the quantity of ions in solution was reduced by 28 days and remained largely unchanged for the duration of the experimental period. From these observations and the calculations shown in Table 5.10, the slag had little positive hydroxyl ion removal capacity and appeared to achieve its pore solution ion reduction by diluting the cements alkalis. However, the slag was generally unable to provide the reductions expected by a zero alkali cement and appeared to contribute small quantities of hydroxyl ions to the pore solution. This contribution had an increasingly greater effect on the quantity of ions in solution as the alkali content of the cement decreased. A similar effect was observed with the ion concentration. The increase dilution effect created by the reduced water demand of the slag was not sufficient to overcome the contribution of ions from the slag.

Overall the water demand of the slag was greater than that of the ash. The presence of the increased free water content and its dilution effects did not appear to have such an important role in the ion reduction mechanism as seen with the pfa. The slags appeared to act primarily as neutral filling material which itself possessed cementitious qualities - effectively a low alkali cement.

The effect of slag substitution on the potassium ions in solution was similar to that observed for the hydroxyl ions. Each slag cement blend was able to reduce both the quantity of ions in solution and their concentration, except when cement A was replaced by 40% slag. The reduction in the quantities of ions in solution was largely achieved by the time of the 28 day measurement, and for cements B, C and D approximated to ion quantities expected by alkali dilution, as shown in Figures 5.17 and 5.18. Although there was some movement of potassium ions thoughout the experimental period, the effect of the slag appeared to be relatively neutral. When account of the ions removed by cement hydration was considered the slag appeared to contribute some potassium ions to the solution (Table 5.11) with time.

The proportions of potassium ions in solution shown in Tables 5.7 to 5.9 were calculated based on the total quantity of potassium available from a gramme of each cement. As such, the reducing proportion of potassium ions in solution with increased slag substitution, reflects the reducing cement content and would indicate the neutral effect of the slag content. The influence of the slag portion may be better examined if the total ion quantity per gramme of cement was reduced proportionally with the cement content, i.e. to 60, 40 and 20%. As shown in Table 5.13, the proportion of potassium ions in solution remained at reasonably fixed proportions of the cement content at each age, confirming that the slag has little positive potassium ion removal properties.

The partial replacement of each cement by slag had only limited influence on their ability to reduce the measured ionic concentrations and the quantity of sodium ions in solution. The overall sodium ion concentrations were primarily determined by the sodium content of the cement used. Although the addition of slag generally was able to reduce the sodium ion concentration this appeared to be largely a function of the greater free water content. When this dilution effect was taken into account then the reductions achieved were extremely limited. Figures 5.17 and 5.18 demonstrate these reductions in comparison to the effects expected by alkali dilution. As with previous ion species most of the measured reduction occured before the 28 day measurement with little subsequent ion movement thereafter. From the figures the addition of slag was generally unable to reduce the quantity of sodium ions in solution,

. However, it was apparent that quite

considerable quantities of sodium had been released from the slag and/or were not removed by the hydration process. Table 5.14 provides some indication of the proportion of ions in solution estimated to originate from the slag proportion of the blended cement. This data was recalculated to provide an estimate of the actual quantity of potassium and sodium ions contributed by the slag in tables 5.15 and 5.16 using the equation shown in 5.3.

Conclusions

1. The high alkali pfa was able to reduce both the concentration and quantity of hydroxyl ions in the pore solutions of cement pastes made with medium to high alkali content cements.

2. The high alkali pfa contributed hydroxyl ions to the pore solution of the paste made with a low alkali cement.

3. The ash was able to achieve some concentration/quantity reductions by 28 days, which were probably attributable to greater quantity of free water being present in the pores. Significant quantities of ions were then removed from solution over the remaining experimental period.

4. Pfa appeared to preferentially remove potassium ions over sodium ions from solution.

5. The blastfurnace slag was also able to make significant reductions in the quantities of ions in solution compared with the effect of an equivalent amount of Portland cement.

6. The slag had achieved most of its reduction by the time of the first measurement at 28 days. There appeared to be little subsequent ion movement thereafter.

7. The slag appeared to act principally as a zero or low alkali cement. However, it appeared that some sodium ions were released into solution over the duration of the experiment.

CHAPTER 6

Pore Solution Composition of Blended Cements: Replacement Material Variables

6.1 Introduction

The previous chapters have examined the influences that the cement's alkali content had on the pore solution composition when used to produce pastes, mortars and concretes. The scope of this work was then broadened to assess the importance of the cements' alkali content when it was blended with various proportions of a reference ash and slag. From this work it was concluded that these replacements were only able to provide beneficial alkali removal properties when blended with the moderate or high alkali content cements (B,C and D), and actually contributed alkalis when blended with the low alkali content cement (A). It was apparent that the two materials achieved their alkali ion reduction in different ways. The slag acted mainly as an inert (low alkali) filler which achieved a large part of its reduction by the time of the first measurement at 28 days. In comparison, the pfa continued to remove ions up to the final measurement made after one year. However, it appeared that the ash did release some alkali into the pore solution, which may have reduced the ash's full alkali sorption capacity.

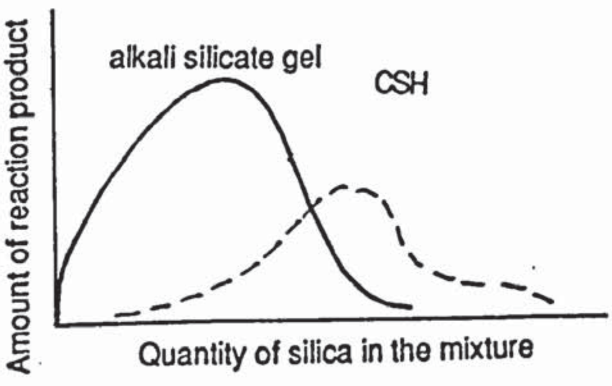
The work in this chapter was designed to establish what effects, if any, the alkali content and/or other physical properties of pfa's and gbfs's had on their alkali removal capacity. As previously described, ashes and slags may contain considerable quantities of total alkali. Therefore it was clearly important to determine whether a relationship existed between the alkali content of a replacement material and its effectiveness as an alkali remover, in blended cement specimens.

The pore solutions were expressed from blended cement paste specimens which were produced by replacing a single reference cement in turn by a range of four pfa's and 3 slags. The replacement materials were selected to represent a wide range of total alkali contents, fineness (in the case of the pfa's) and methods of manufacture (in the case of the slags).

6.2 Previous Work

The work reported in 5.2 briefly reviewed previous studies on the effectiveness of various materials as cement replacements with respect to alkali ion removal. These studies were presented together with the current hypotheses on the possible mechanisms by which the materials effect these reductions. In this chapter interest has been focussed on the role of the alkalis present within the replacement materials, in relation to their performance in controlling expansion due to ASR.

Nixon and Gaze(40) reported that mortar bars made with Beltane opal as the reactive aggregate in mixes containing 10 or 20% of a high alkali pfa resulted in expansions greater than those of control mixes which contained no pfa. When the same cement was substituted by 30% of the same ash, the expansion was suppressed. In contrast, when a low alkali ash was used, only 20% cement replacement was required to achieve effective suppression. Urhan(115) provided some explanation for this phenonemon. A cement of given alkali content partially substituted by a pozzolanic material could depending on the proportion replaced result in an increased quantity of CSH being produced. The excess silica present reacts with the hydroxyl ions in solution reducing its pH and the rate of dissolution of the silica. This favours the pozzolanic reaction. Inadequate additions of pozzolanic material which provide insufficient silica to achieve this effect may then result in an increased quantity of alkali silicate gel being formed, thus increased expansion potential see Figure 6.1(115).



(arbitrary units)

Fig 6.1 Relationship between the amount of reaction product and quantity of silica in mixture from reference 115.

Several workers who have studied the influence of various replacement materials on the pore solution composition (see 5.2) have noted variable effectiveness in alkali removal properties which would support Urhan's(115) views. However, there is some evidence also to suggest that the alkalinity of both the replacement material and the cement replaced influence their performance.

Glasser and Marr(38) demonstrated the influence of alkali content by replacing two cements, having equivalent soda contents of 0.51 and 0.95% with a high alkali content and a low alkali content pfa 3.6 and 1.2% equivalent soda respectively. Their work demonstrated that both the high and low alkali content pfa's were capable of reducing the hydroxyl ion content of higher alkali cements' pore solution. However, when blended with the low alkali cement, only the low alkali pfa was able to provide some reduction, while the higher alkali pfa contributed to the alkalinity of the pore solution. This effect was similar to that reported in Chapter 5 and previously published by Nixon et al(116).

Diamond(106) studied the influence that two Danish flyashes had on the pore solution of a cement paste after curing periods ranging from four hours to 174 days. He noted that for their most part pfa's acted as inert diluents but recognised that they can vary considerably in availability of alkalis and in reactivity.

Kollek et al(105) related the expansion of mortar bars to the pore solution composition of various blended cement specimens. They reported that the pfa's tested (0.97 and 3.17% equivalent soda) generally were able to reduce the hydroxyl ion concentration of the pore solution when blended with a high alkali Portland cement (0.92% equivalent soda), but the high alkali pfa made a small positive contribution when combined with the low alkali cement (0.34% equivalent soda).

Less information has been published about the effects of blastfurnace slags on pore solution composition. Glasser and Marr(38) concluded from their study that their effect was broadly neutral with respect to alkali removal, and that they achieved their effect largely by alkali dilution. Kollek et al(108) reported similarly, but recorded small contributions to the pore solution hydroxyl ion concentration above those expected by alkali dilution. The contribution depended on the alkali content of the slag and its reactivity. Therefore, although most pozzolanas contain considerable quantities of alkali most of these are bound in the glassy structure of the pozzolana and only a small proportion is soluble in water and appears in the pore solution. The water soluble alkali content of flyash is usually less than 0.1% equivalent soda(112). However, recent literature demonstrates that the alkalis combined in the vitreous structures of the pfa which were previously thought not be be involved in the hydration reaction of the pozzolana are released by the pozzolanic reaction. It is not known what quantity of alkalis participate in the reaction, or how the released alkalis are distributed between the hydrated solid phases and the pore solution. Experimental observation by Hobbs(117) and Glasser and Marr(38) have recently shown that considerable quantities of alkalis may be leached out of pfa and slag blended concretes. As such the present consensus of opinion on replacement materials now considers their alkali content of some importance when assessment of their suitability for reducing the risk of ASR is made.

For practical situations, it is currently suggested that the water soluble alkali content of any pozzolana used as a cement replacement material be included in any calculation relating to reactive total alkali content of concrete(81). Limits have been placed on the alkali content of slag blended cements. The German standard DIN 1164 requires slag blended cements containing at least 50% slag to have an acid soluble alkali content for the blend below 1.1% equivalent soda. When the blend contains at least 65% slag the blend may contain up to 2% equivalent soda. In Britain, it is recommended(81) that the slag blended cements containing at least 50% slag may be considered equivalent to a Portland cement of 0.6% equivalent soda, provided that the acid soluble alkali content of both the Portland cement and the slag is less than 1.1%.

6.3 Experimental Procedure

The experimental data for the work in this chapter was generated by analysis of pore solutions expressed from a range of blended cement paste specimens, produced by partially replacing cement B, 0.67% equivalent Na_2O with a series of four pfa's and three slags.

Each ash was used in turn to substitute the Portland cement by 20% and 40% and the slags were used at 40% and 60% by weight of cement. In addition a control mix was also produced which contained no cement replacement. A water to (cement + replacement) ratio of 0.45 was maintained for each specimen and no account was taken of reduced water demand created by the replacement materials. The cement pastes were cured in sealed cylindrical containers at 20°C for 28, 84, 168 and 365 days.

At the appropriate curing age triplicate specimens were demoulded and samples of their pore solution were expressed and analysed for hydroxyl, potassium and sodium ion concentrations as described in 2.2.2 and 2.2.3. The unbound water content of each specimen was estimated using the method described in 2.2.4.

The full chemical composition and physical properties of the replacement ashes and slags are shown in Tables 2.3, 2.4 and 2.5. However, a brief summary of the main characteristics of the materials is shown below;

Pfa 2.	High alkali, fine ash	3.37 % eq Na_2O
Pfa 3.	High alkali, coarse ash	3.20 % eq Na_2O
Pfa 4.	Low alkali, fine ash	1.04 % eq Na_2O
Pfa 5.	Low alkali, coarse ash	0.97 % eq Na_2O
Slag 1.	Granulated slag	0.97 % eq Na_2O
Slag 2.	Pelletized slag	0.74 % eq Na_2O
Slag 3.	Granulated slag	0.60 % eq Na_2O

The data recorded from the specimens has been presented in Appendix 6, in two parts. Firstly, those results and their graphical interpretation for the pfa blended specimens are presented in Tables 6.1 to 6.3 and Figures 6.2 to 6.9. Secondly, the results and Figures associated with the slag blended specimens are presented in Tables 6.4 to 6.6 and Figures 6.10 to 6.17. The measured ionic concentrations were analysed and presented using similar calculations to those shown in 4.3.

6.4 Results and Discussion

6.4.1 Pulverized Fuel Ash Replacements

The primary objective of the work in this chapter was to examine the influence of the ash's alkali content on the pore solution of a reference cement. The findings of previous workers suggested that high alkali pfa's had reduced alkali ion removal capacities. The data in this chapter confirmed that the alkalinity of the ash was a major factor in the determination of the general quantity of alkali ions removed from the pore solution, but was not the sole factor. Figures 6.2 and 6.3 demonstrate graphically the effect each pfa had on the quantity of hydroxyl ions in solution as a function of time. Each figure also has two reference lines (denoted C and C') corresponding respectively to the quantity of hydroxyl ions measured in the control solution and the ion quantity calculated to exist had the cements' alkalis been diluted by an inert material.

The changes in the pore solution hydroxyl ion quantity were generally similar to those of ash blended specimens in Chapter 5. That is at 28 days every ash at both replacement levels was neutral or contributed hydroxyl ions to the pore solution when compared to the ion quantity expected solely by alkali dilution. Thereafter all showed continued ion removal up to 365 days. However, certain variations in this trend were apparent. The lower alkali ashes tended to quickly remove ions from solution up to 168 days and then at a slower rate thereafter. In contrast the high alkali ashes appeared to steadily remove ions throughout the entire experimental period. By 365 days all ashes at both replacement levels had achieved hydroxyl ion quantites below the expected C' value. From their removal characteristics the ashes were readily differentiated into high or low alkali contents as shown in Figures 6.2 and 6.3. The low alkali ashes at each replacement level quickly achieved the expected alkali dilution value (C') and removed significantly greater quantities of ions than the higher alkali ashes. From the measurements of total hydroxyl ions removed between 28 days and 365 days by each ash (per gramme of blended cement) shown in Table 6.3 it was confirmed that the higher alkali ashes were unable to remove as many ions as the lower alkali ashes. It was also apparent that the ability of each ash to remove hydroxyl ions from solution was reduced by approximately half when its inclusion proportion was doubled from 20% to 40%. From these observations the pfa became an increasingly inefficient remover of hydroxyl ions as the inherent or the total alkali content of the ash rose. As seen in Figures 6.2 and 6.3 even the inefficient pfa's, those with high alkali contents were able to produce hydroxyl ion quantities which approximated to those expected by an inert material (C'). This suggests that principally each pfa acted as 'a low alkali cement' which provided some alkali dilution effect. However, the quantity of ions removed by the pozzolanic reaction was influenced by the release of alkali ions from the ash. Therefore the positive ion removal capacity is partially offset by the quantity of alkali ions released by the ash.

Although these results indicate that the alkalinity of the pfa appears to be of primary importance in the determination of the ash's effectiveness as an ion remover, the physical particle size of the ash may also influence the effectiveness to a lesser extent. The low alkali fine ground ash, pfa 4 proved to be more effective in removing hydroxyl ions when used to replace both 20% and 40% of the cement than the coarser ash, pfa 5, which had a lower alkali content. However, the higher alkali ashes were not as readily classified in this respect. When included as a 40% cement replacement the finer ground ash, pfa 2 was able to remove more hydroxyl ions than the lower alkali coarser ash, pfa 3. Although the reverse trend was observed when ashes 2 and 3 were included at 20%. The finer ashes in all cases did enable a larger initial ion reduction at 28 days. Possibly this effect is due to the finer particles providing a greater reactant surface area and so reducing the hydroxyl ion concentration faster per unit of silica present(115).

Urhan(115) reported that finely divided pozzolanic materials may form a greater quantity of hydrate and develop a greater mechanical strength than coarser materials. Although the smallest grains of silica would hydrate first, larger grains progressively being hydrated as a function of time would suggest that the particle size distribution may indicate the potential reactivity of the flyash, Mehta(67) found that the size distribution alone was not a sufficient guide, and account of the mineralogical composition should be taken.

The pfa's used in this study were all low calcium content ashes, which consisted principally of a slow reacting aluminosilicate glass spheres, ranging in size from under 1μm upto 100μm. The mineralogical composition of each was thought to be largely amorphous. However, the presence of crystalline materials in the glass due to partial devitrication during production/manufacture may reduce the reactivity of the ash(118). It was possible that variations in the mineralogical composition of the ashes could have influenced their ion removal behaviour. However, the time and techniques required to examine the variations in performance due to the mineralogical composition were beyond the scope of this project.

When the reference cement was blended with the ashes the quantities of potassium ions in solution were reduced to values well below those expected by the dilution of the cement's potassium content. Figures 6.6 and 6.7 demonstrate the quantity of potassium ions in solution as a function of time, together with the reference lines C and C'. As seen with the hydroxyl ions, the alkalinity of the ash appeared to determine the ability of the ash to remove potassium ions. The lower alkali ashes had a larger ion removal capacity, with the finer ashes providing slightly better properties to the ash. The alkalinity of the ash had a dramatic effect on the quantity of sodium ions in solution, as shown in Figures 6.8 and 6.9 The ashes were distinctly grouped into high or low alkali content ashes. The high alkali ashes, pfa's 2 and 3 contributed sodium ions to the pore solution producing an ion quantity in excess of the control specimen. In contrast pfa's 4 and 5 had considerably lower inherent sodium contents and were able to reduce the quantity of sodium ions in solution to a level below that expected by dilution of the cement's sodium ion content.

From the Figures 6.5 to 6.8 and the quantities of ions removed between 28 and 365 days by each ash shown in Table 6.3, it was apparent that the potassium ions were being removed from the pore solution preferentially to sodium ions. The potassium ions were removed from solution during the first 168 day period, followed by little if any ion movement thereafter. In comparison, the sodium ions in solution with the exception of pfa's 4 and 5 at 20% replacement did not demonstrate much ion movement throughout the entire experimental period.

The mechanism by which the pozzolanic materials remove ions from solution and combine them into the hydration structures has been attributed mainly to the reaction between the silica present in the pfa and the calcium hydroxide from the cement. The excess of silica present in the ash has been reported as being able to modify the composition of the CSH gel, reducing the ratio of calcium to silicon (C/S) present.(38,111). This low ratio CSH gel has greater alkali sorptive properties. Glasser and Marr(38) using electron analytical techniques found that the C/S ratio of the CSH phase could range between 0.8 and 1.7 corresponding to silica saturated and lime saturated respectively. Plain cements had C/S ratios typically close to 1.7, however when various siliceous replacement materials were used to partially replace the cement the composition of the CSH phase changed. The CSH became silica enriched and was able to produce a ratio of 0.8 - 0.9 when silica fume was added. Further additions of silica resulted in unconsumed silica existing with the silica enriched CSH. Rayment(119) reported that after eight days a 20% substitution of a high alkali cement by a low alkali pfa reduced the C/S ratio of the CSH phase from 1.71 to 1.55. At the same time the potassium content of the CSH rose from 0.58 to 0.76% Glasser and Marr(120) also noted that the strength of sorption of the CSH decreased in the order of caesium > potassium > sodium, which may explain the preferential removal of potassium ions from the pore solutions in this work. They also explain that the different ability of CSH gels to incorporate potassium ions is based on the electrical charge of colloidal particles. At a high C/S ratio the charge is positive, at a low C/S ratio the charge is negative. The sign of the electrical charge depends on the relative availability of cations and anions.

It appears from previous workers findings(119) that pfa is capable of forming some low ratio CSH gel, but the increased alkali binding capacity is limited by the comparatively large release of alkali into the pore solution by the ash and partly due to kinetic reasons(38,120). Therefore, the alkali content of the ash used and its total replacement proportion appears to be primary importance when assessing the overall effectiveness of the ash as an alkali ion remover.

6.4.2 Ground Blastfurnace Slag Replacement

The effect on the quantity of hydroxyl ions in the pore solution when the reference cement was blended with slags of various alkali content as a function of time are shown in Figures 6.10 and 6.11. The figures also include the quantities of ions measured in the control pore solution and the calculated ion quantity assuming replacement by a zero alkali cement and are denoted C and C' respectively.

Each slag was able to reduce the quantity of hydroxyl ions in solution below that of the control solution. However, only slag 2, the medium alkali pelletized slag was able to reduce the quantity of ions below the expected alkali dilution value C' at either replacement level. Slags 1 and 3, the granulated high and low alkali content slags, had achieved their ion quantity reduction by the 28 day measurement and removed very few ions over the remaining experimental period. Slag 2 achieved a considerable reduction in ions by 28 days and continued to remove a modest quantity of hydroxyl ions over the duration of the experiment. The relative performance of each slag indicated that the slags acted primarily as low alkali cementitious materials which provided a useful dilution of the cements' alkalis. The slags tested were not particularly efficient alkali ion removers, the variations in performance were possibly more closely associated with the reactivity of the slag rather than its alkali content.

The effect on the quantity of potassium and sodium ions in the pore solution that blending the slags with the reference cement had are shown in Figures 6.13 to 6.18. All three slags were able to reduce the quantity of potassium ions at both levels of replacement to values approximating to those expected by alkali dilution. The higher potassium content slag 1, was unable to reduce the quantity of ions below the expected C' value and appeared to release some ions into solution with time. Slags 2 and 3 reduced the quantity of ions below the expected C' value, both removing small quantities over the experimental period. As observed for the hydroxyl ions, the reduction

in ion quantity was largely achieved by the time of the first measurement with little movement of potassium ions into or out of solution thereafter. In contrast the addition of slag to the reference cement was unable to reduce the quantity of sodium ions in solution significantly below that of the control solution. Slags 1 and 3 actually contributed sodium ions to the solution resulting in ion quantities greater than the control. Each slag released small quantities of sodium ions into the solution as the experimental period passed, with the exception of slag 3 at 60% replacement. It was
LL apparent from Table 6.6 that the larger replacement proportion of slag generally resulted in better ion removal properties between 28 and 365 days. This trend was observed for each ion species and a trend contary to that observed for the pfa blended specimens.

When the pore solution effects achieved by the slags are compared to those of the pfa's, it is noticeable that the slags tend to have achieved all or most of their ion reductions by 28 days. The pfa's generally require the entire experimental period to remove ions. This is probably due to differences in their chemical composition. The slags contain comparatively large quantities of calcium and possess a highly reactive glass structure. Under normal conditions slags may produce cementitious products after 3 days, therefore by 28 days a considerably greater proportion of slag would have been hydrated than the slowly reacting low calcium content pfa's. For the remainder of the experimental period the slag specimens behaved essentially as inert materials and were unable to remove large quantities of alkali from solution. Unlike pfa, slags generally have considerable calcium contents and C/S ratio's close to unity. Therefore large quantities of slag would be required to modify the CSH gel and increase its alkali sorptive properties(38). This modification of the CSH gel may provide some explanation for the slightly improved alkali ion removal performance for the slag at 60% replacement as detailed in Table 6.4. Although Harrison et al(12) reported slight reductions in the C/S ratio of CSH gels made with slag cements, it would appear that the benefits of its inclusion are more likely to be attributable to the greater quantity of CSH formed, its denser microstructure and its relatively low water soluble alkali content.

The performance of each slag in reducing the quantity of alkali ions appeared to be influenced largely by the method of slag production and to some extent by its alkali content. The manufacture of the slags varies principally in the way the molten slag is quenched. This may be achieved by the use of water which produces a granulated slag of water and air which produces pelletized slag. The method of quenching molten slag has been previously found to influence the effectiveness of slag in suppressing ASR expansion(122). Normally the water quenching method produces slags of greater glass content. However, there is evidence to suggest that the overall reactivity of the slag may depend on the degree of the glass disorder rather than the glass content(67). From the data recorded differences in the slags reactivity appear to be equally as important a factor as their alkali content.

6.5 Conclusions

1. The alkali content of pfa is an important factor, but not the sole factor in determining its ability to remove hydroxyl ions from the pore solution. The fineness of the ash also appears to have an effect.

2. The more effective ashes, those of low alkali content were able to reduce the quantity of hydroxyl ion in solution to a level well below that expected by dilution of the cements alkalis. The least effective ashes were able to produce ion quantities comparable to alkali dilution.

3. Pfa's preferentially removed potassium ions from solution over sodium ions.

4. The ion removal capacity of pfa decreased as its alkali content rose or replacement proportion increased.

5. The blastfurnace slags were not efficient alkali ion removers and achieved their ion reductions largely by their neutral effect diluting the cements alkalis.

6. The ability of slags to reduce the quantity of ions in solution is influenced by the slags' reactivity, possibly due to its manufacture process and to some extent by its alkali content.

7. The larger additions of slag had improved ion removal properties measured between 28 and 365 days than when included at lower replacement levels.

CHAPTER 7

The Effect Of Alkali Salts On The Pore Solution Composition

7.1 Introduction

Several workers have previously noted that alkali salts added to concrete were able to increase the alkalinity of the pore solution. It is possible that alkali salts such as sodium chloride which may be present in concrete as a contaminant from sources such as dredged aggregates, deicing salts or ground/sea water could initiate or increase the risk of ASR. The mechanism by which the quantity of hydroxyl ions in solution is increased is thought to be due to complexation of the chloride ions by the aluminate phases of the cement.

The work in this chapter was intended to measure the complexing ability of a cement and determine to what extent the alkalinity of its pore solution was increased, when sodium chloride was introduced via the mixing water.

7.2 Previous Work

It has been demonstrated both by expansive mortar bar measurement and by examination of the pore solution composition, that the addition of alkali salts to cement can raise the alkalinity of the pore solution. Gaze and Nixon(40) used potassium sulphate additions in conjunction with a low alkali cement to produce expansive mortar bars. They found no expansion when the cement was used without sulphate addition, but recorded increasing expansions as potassium sulphate was included. Mehta(67) reported similar findings when he added sodium chloride to a low alkali cement (0.42% equivalent soda) to produce mortar bars having an equivalent soda content of 0.92%.

Roberts(28) studied the effects of corrosion inhibitors sodium nitrite and sodium benzoate on the alkaline environment of Portland cement pastes by the examination the cement's "mix water". He produced Portland cement pastes of high water cement ratios, typically between 1 and 2. Various quantities of different admixtures were included in the pastes which were kept agitated to maintain the mixture as a slurry. This allowed removal of liquid for chemical analysis for up to seven days. From this it was apparent that the concentration of the admixed anions were reduced within the first few days due to reaction with the tricalcium aluminate in the cement to form complex hydrated calcium aluminate salts. A by-product of the reaction between sodium nitrite or benzoate and cement was sodium hydroxide.

Holden et al(108) demonstrated that the pore solution hydroxyl ion concentrations of cement pastes could be enhanced by the addition of sodium chloride (0.4% Cl^- by weight of cement). The hydroxyl ion concentration of the pore solution was further enhanced when sodium sulphate was added in addition to the sodium chloride. They reported that the hydroxyl ions in solution were a product of the reaction between the alkali chlorides and the aluminate phases of the cement. The quantity of hydroxyl ions in solution was largely determined by the tricalcium aluminate content of the cement(108,123).

The reactions between alkali salts of various sorts and C_3A are thought to be similar to that of the alkali sulphates normally present in cements and C_3A, which results in the precipitation of calcium sulphoaluminate and enriches the pore solution with sodium, potassium and hydroxyl ions. Thus if the cement contains alkali chlorides a reaction which produces a calcium chloro aluminate complex may result and hydroxyl ions are released into the pore solution.

There has been less work published on the effects of alkali salts introduced into mature concretes from external sources. It has been reported in Denmark that some concrete road slabs made using a low alkali cement, but exposed to deicing salts had been extensively attacked by ASR. Chatterji(131) who investigated this problem, found that hardened mortar cubes containing reactive aggregate and exposed to a saturated sodium chloride solution at 50°C expanded. In contrast, those cubes made with an inert aggregate did not expand. This method now forms the basis of a regularly used test method in Denmark.

From the previously reported findings there is no doubt that sodium chloride does increase the quantity of hydroxyl ions in solution to an extent which may be sufficient to induce expansion due to ASR. However, at present there is little quantitative information about this effect.

7.3 Experimental Procedure

The experimental data for the work in this chapter was obtained from the pore solutions expressed from three series of cement paste specimens. Each series of specimens was batched and mixed as described in 2.2.1 using a water cement ratio of 0.47. For each series two sets of triplicate specimens were made and cured in airtight containers for 28, 56, 84, 168 and 504 days; one set at 20°C, the second set at 38°C.

The first series of specimens was produced from four plain Portland cements B, C, D and E which had equivalent soda contents of 0.67, 0.86, 0.94 and 1.06% respectively. These specimens had no alkali salt added and served as a reference series against which the other two series could be compared.

The second series of specimens was made using cement B with appropriate additions of sodium chloride to the mixing water. Sodium chloride was added in amounts calculated to reproduce the equivalent sodium oxide contents of the plain cements employed in the first series, together with an additional intermediate mix of 0.775% equivalent soda.

The third series contained cement B with additions of synthetic seawater (SSW) at levels calculated to reproduce the alkali contents of the reference cements plus the additional intermediate mix. The calculation of the quantities of sodium chloride and synthetic sea water are shown in Appendix 7.

The pore solutions were expressed and analysed for hydroxyl, potassium, sodium and chloride ion concentrations using techniques described in 2.2.2 and 2.2.3. The evaporable water contents of the specimens were also determined as described in 2.2.4. The experimental data obtained are recorded in Tables 7.1 to 7.10 with graphical interpretations of this data shown in Figures 7.1 to 7.10 located in Appendix 7.

7.4 Results and Discussion

The quantity of hydroxyl ions in solution for the neat cement specimens cured at 20°C increased with the alkali content of the cement. The quantity of hydroxyl ions in the pore solutions of specimens to which NaCl or SSW was added also increased approximately in line with the calculated alkali level. Those specimens with pure NaCl additions produced ion quantities which correlated reasonably closely with those of the neat cements, while the SSW specimens consistently produced a greater quantity of hydroxyl ions in solution, as shown in Figures 7.1, 7.3, 7.5 and 7.7. The relative differences between the ion quantities of the three series were generally maintained throughout the experimental duration.

It was thought that the greater quantity of ions produced by the SSW specimens was due to the formation of additional alkalis due to the presence of small quantities of sodium and potassium sulphates within the seawater powder. Holden et al(108) have reported significant increases in the hydroxyl ion content of pore solutions from specimens containing added sulphates. The increase in ion content for these specimens and those with pure NaCl additions was relatively even in proportion with the amount of added alkali salt. In contrast the neat cement specimens produced a more eratic increase in ion quantity with increased alkali content. This was also observed in the work reported in Chapter 4 and possible explanations for this variance have been described in 4.4.

When the specimens were cured at 38°C the quantity of hydroxyl ions measured in the pore solution of each series were consistently lower than equivalent specimens stored at 20°C, as shown in Figures 7.2, 7.4, 7.6 and 7.8. Although trends observed for the neat cement specimen at 20°C were also observed at the elevated curing temperature, it was apparent that the chloride ion complexing ability of the cement was reduced. This was previously reported by Roberts(28). The quantity of hydroxyl ions produced by specimens containing pure NaCl additions still correlated well with those of the neat cement specimens. However, those containing SSW appeared to show little evidence of increasing ion quantity. This apparent exhaustion of the chloride complexing ability remained constant over the entire experimental period and was accompanied by comparatively large quantities of free chloride ions present in the pore solution.

The reduction in the recorded hydroxyl ion content of the neat cement specimens stored at 38°C may be due to modified hydration as a result of the elevated curing temperature. Previous workers(76) have recorded strength losses for concretes subjected to similar elevated curing temperatures, which was attributed to retardation of the long term hydration phases of the cements.

In the pastes with added chloride the quantity of free chloride ions in solution complemented the observed trends of the hydroxyl ions. From these observations recorded in Figures 7.1 to 7.8 the chloride ion content was higher in specimens stored at 38°C than at 20°C which suggested that the stability of the chloroaluminate complex was reduced at the elevated curing temperature. Further, the tailing off in the rate of hydroxyl ions produced by increased additions of SSW, accompanied by the sharp increase in free chloride ions measured in solution when stored at 38°C also suggests that the complexing ability of the aluminate phase in the cement was exhausted.

The quantity of sodium ions in solution increased by relatively small amounts as the alkali content of the neat cement increased. In contrast, as NaCl was introduced the quantity of sodium ions increased by large amounts. The actual quantity of sodium ions in solution for each inclusion level remained relatively constant over the experimental period, the values recorded in Tables 7.1 to 7.10 with graphical interpretations of typical sodium ion quantities in solution shown in Figures 7.9 and 7.10.

It was apparent that the quantities of potassium ions present in the pore solutions of specimens with added alkali salts were reduced. A greater reduction of ions was observed for the SSW specimens than for the pure NaCl specimens. The reduction in potassium ion achieved by the SSW specimens was greater at 20°C than at 38°C. The pure NaCl additions produced the same or a slightly greater quantity of potassium ions than the plain reference cement. Therefore, it would appear that at least some of the potassium from the cement was taken out of solution by the chloride complexing reaction. In Tables 7.1 to 7.10 it was noted that the quantities of anions and cations did not balance exactly, although generally they were within a 5% tolerance. The variance recorded may be due to imperfect callibration standards, the higher concentration pore solutions lying off the linear part of the flame photometer scale and/or suspended particulate matter affecting analyses.

In parallel experimental work carried out at the Building Research Station, equivalent mortar bars to the pore solution specimens were produced for expansion measurements. Both series of specimens with added salt produced expansions which correlated quite closely to the expansions measured for the control neat cement specimens (see Figure 2 in Sodium chloride and alkali aggregate reaction paper in Appendix 8). The trends in expansion were influenced by the quantity of hydroxyl ions in solution and were generally in accordance with the findings reported for the pore solution composition. The work carried out at BRE is reported in greater detail in the paper 'Sodium chloride and alkali aggregate' in Appendix 8.

7.6 Conclusions

1. The introduction of sodium chloride into a cement paste at the mixing stage resulted in an elevation in the concentration and total quantity of hydroxyl ions in the pore solution.

2. This increase was attributed to the tricalcium aluminate phase of the hydrating cement reacting with a proportion of the chloride ions:
$4CaO.Al_2O_3.19H_2O + 2NaCl \rightarrow 3CaO.Al_2O_3.CaCl_2.10H_2O + 2NaOH + 8H_2O$.

3. The increase in pore solution hydroxyl ion concentration could be approximately predicted by the total conversion of the chloride added ions to the mix water.

4. The complexing ability was reduced at the elevated curing temperature of 38°C due to the instability of the chloroaluminate hydrate at the elevated temperature.

5. Equivalent mortar bars containing added alkali salts produced expansions which correlated reasonably closely with the quantity of hydroxyl ions in solution.

CHAPTER 8

General Conclusions and Recommendations For Further Work

8.1 Conclusions

This thesis has reported on various studies related to the control of ASR by blended cements. From this work the following conclusions were drawn:

1. Under the experimental conditions described in Chapter 3, the rate at which ASR was induced appeared to follow a second order dependence on the hydroxyl ion concentration for plain cements and those containing up to 40% pfa or slag. However, when cement blends included 60% slag the rate exhibited a first order dependence on the hydroxyl ion concentration. It is suggested that in the former case the ASR process was subject to reaction controlled kinetics and in the latter case to diffusion controlled kinetics.

2. Expansion could be induced in specimens subjected to relatively low alkali concentrations, provided unlimited quantities of alkali were available. This suggests that the concentration of the pore solution influences the speed at which the reaction is induced, while the quantity of alkali ions available determines the severity or extent of the reaction. It was thought that the specimens subjected to low concentrations (pH 13) did not expand over the experimental period due to the absence of a positive diffusion potential, i.e. the pore solution alkali concentration of the mortar was larger than that of the curing solution, which appeared to be the primary method of alkali ion transport.

3. The pore solution hydroxyl ion concentrations of both cement pastes and mortars were related by linear functions to the alkali content (eq Na_2O) of the cement used. Therefore, the use of a low alkali content cement (below 0.6% eq Na_2O) as a method of limiting the pore solution hydroxyl concentration is valid. However, from the work carried out in

Chapter 3, merely reducing the hydroxyl ion concentration may not always be sufficient to avoid long term reaction. The cement content of the mix is also relevant as that determines the total quantity of alkali ions available in the pore solution of concrete.

4. The pore solutions expressed from the concrete specimens demonstrated that limitation of the concrete's total alkali content (Kg $eqNa_2O/m^3$) was an effective means of reducing both the concentration and quantity of alkali ions in solution. These specimens emphasized the influence of the concrete mix design and in particular the importance of the water and cement contents. In the context of use with British aggregates which are of only moderate reactivity, either alkali limitation method would probably be sufficient to prevent ASR. However, the method which limits the total alkali content of concrete provides a more flexible means of achieving the limit and would also impart greater long term protection in higher risk ASR environments.

5. The high alkali content pfa (pfa 1) when blended with cements released a proportion of its alkali into solution. This release was smaller than that of the higher alkali cements and caused some reduction in the pore solution hydroxyl ion content when used with medium and high alkali cements. When a low alkali cement was used, however, substitution with the pfa tended to increase the hydroxyl ion concentration.

6. The effectiveness of pfa's in reducing the quantity of alkali ions present in the pore solution was primarily determined by their alkali content, although fineness also had some influence. The low alkali content ashes were the most effective in reducing the pore solution alkali content of cement pastes.

7. The pfa's were able to reduce the pore solution hydroxyl ion content by several mechanisms. It was observed that these mechanisms were essentially those of dilution of the cements alkalis, which was achieved relatively quickly and a long term mechanism which removed ions throughout the experiment period. The long term alkali ion removal

mechanism was thought to be due to sorption into the CSH gel structure. The presence of large quantities of silica from the pfa reducing the calcium to silica ratio of the CSH gel is believed to increase its potential to absorb greater quantities of alkali ions. The large release of alkali from the higher alkali content ashes reduced their dilution effect and also partially countered the effect of the increased alkali ion sorption by the modified CSH.

8. The effectiveness of slags in reducing the alkali ions present in pore solution appeared to be influenced by their reactivity due to manufacture, rather than their alkali content.

9. It was apparent that the slags acted principally as low alkali cementitious materials which diluted the cement's alkalis. The reductions in ion concentration were achieved rapidly, but relatively few ions were actually removed from solution at times longer than 28 days. It was thought that the limited ability of slags to remove alkali ions from the pore solution was due to their calcium to silica ratio being close to unity. Therefore, large additions of slag would be required to modify the CSH gel making it more receptive to alkali ions.

10. From the work with pfa's and slag's, it appeared that control over ASR may be achieved both by physical (reduced permeability) and chemical (reduced pore solution alkalinity) means. The relative importance of each mechanism in the overall control of the reaction appeared to depend on;

1. The type of replacement material used.
2. The alkali content of the replacement material.
3. The replacement proportion.
4. The alkali content of the cement to be replaced.

11. Sodium chloride, a common contaminant of concrete materials significantly increased the pore solution hydroxyl ion concentration of cement pastes. This was a result of the alkali metal chloride's being complexed by the C_3A phase of the cement to form hydrated calcium chloroaluminate and releasing hydroxyl ions into solution.

12. It was possible to calculate the increase in hydroxyl ions in solution due to the addition of small quantities of sodium chloride based on the total conversion of the sodium chloride to equivalent sodium oxide. When large quantities of sodium chloride were included, however, the hydroxyl ion content reached a ceiling level and the pore solution became increasingly enriched with chloride ions. This suggested that the complexing ability of the cement had been exhausted. The complexing capacity of the cement was reduced when the specimens were cured at 38°C, this reduction was attributed to the instability of the chloroaluminate hydrate at the elevated temperature.

13. When sea salt was introduced into the mix, the pore solution hydroxyl ion contents observed at 20°C were significantly larger than those produced by sodium chloride additions. This was attributed to the presence of small quantities of sodium and potassium sulphates in the seawater powder, which were able to produce additional alkalis as a result of formation of calcium sulpho aluminate complexes.

14. Parallel work on the effects of sodium chloride and sea salt additions carried out at BRE demonstrated mortar bar expansions which correlated reasonably well with the observed enhancement of the pore solution alkali content.

8.2 Further Work

A considerable amount of work has been published world wide on the subject of ASR. This work provides an extensive database which has catalogued many aspects of the subject. However, surprisingly little work has been reported on ASR in existing structures. In practice, ASR is most likely to be encountered by the construction industry as problems associated with existing structures. There would then seem a demand for future work to address the practical problems associated with established ASR distressed structures. In the author's opinion this work should be primarily directed into developing techniques by which the progress of the reaction may be monitored and used to predict the service life of affected structures. A fundemental step in being able to make these predictions must be to establish the effect that ASR has on the physical/structural properties of concrete. Then it is necessary to establish the relationship between the weakening of the structure and the progress/extent of the reaction. Further, the possibility that the progress of the reaction may be estimated by measuring changes in the pore solution composition of the concrete needs to be examined. If the pore solution changes could be related to the progress of the reaction this may provide a useful monitoring technique on which to base the service life predictions.

It is anticipated that the technique developed for the work in Chapter 3, that of inducing ASR by submersion of specimens in alkaline solutions has the potential for further developement. Using a more realistic "pore solution" it would be interesting to explore the relationship between the concentration and quantity of alkali ions on expansive behaviour and the influence of alkali type on the reaction. In Chapter 3 problems were encountered in relating the observed expansion to steady state diffusion measurements. Further work on this correlation would be useful. This correlation may be better studied if the steady state diffusion measurements were related to the alkali ions being removed from the curing solution by the reacting specimen, rather than its expansion. The technique described in Chapter 3 may also have the potential to be used for other applications, for example, testing aggregates for their potential reactivity. It has been previously reported that some British aggregates have been difficult to assess and the results obtained using American standard tests have proved to be unreliable. The developement of a technique or test method which is more suited to these aggregate types is therefore desirable.

Another future application of the technique would be to examine the effectiveness of proprietary concrete surface treatments claimed to prevent ASR by reduced moisture ingress from external sources. In addition, it would be interesting to establish how much reaction once initiated within a specimen may be sustained after treatment by these coatings. The objective would be to ascertain the length of time and likely expansions, if any, which may be experienced after the treatment has been completed.

It has been established in Denmark that deicing salts used on roads have been the cause of ASR. It would be interesting to examine such concrete to determine whether the reaction in the mature concrete is attributable to an enhancement pore solution alkali content as a result of the complexation of the chloride ion as described in Chapter 7. By sectioning samples and pore solution expression it would be interesting to establish the increase in the pore solution alkali concentration, at various depths below the surface and relate it to the severity of reaction.

The work in this thesis and that of other workers has demonstrated that when pfa's or slags are blended with cements they release some alkali into the pore solution. It would be desirable to establish the proportion of each material's total alkali content and whether the quantity is fixed or varies depending on the hydration environment. If the alkali release properties of replacement materials were better understood then greater benefits with respect to prevention of ASR might be achieved by careful selection of the replacement material and cement combination used. This would be relatively easy if the alkali ions in solution which originated solely from the replacement material could be isolated. One possible method by which this could be done is to blend the replacement material with a simulated hydrating system, made from pure cement minerals. In this way, all the alkalis present in the pore solution would be of known origin, and could be quantified by analysis of the expressed pore solutions. The use of cement minerals and/or known quantities of alkalis would enable various hydration environments to be simulated.

A further study using replacement materials blended with pure cement minerals could be done to clarify the actual quantity and mechanism by which the alkali ions released into the pore solution are incorporated into the CSH gel structure. Previous workers have reported that the large quantities of silica present in some replacement materials were able to modify the CSH gel composition. The resulting silica-rich gels have a greater capacity to absorb alkalis from the pore solution than similar calcium-rich CSH normally produced in plain cements. However, it still remains unclear as to the actual mechanism by which the alkali ions are incorporated into the CSH structure. It is suggested that further studies examining the influence of replacement materials on the composition/structure of CSH gels and the mechanism by which ions are incorporated into their structure might be undertaken by the use of solid state Nuclear Magnetic Resonance (N.M.R) spectrometry. The application of this rapidly developing technique has the potential to provide some insight into the structure of the gel, the bonding of the silicate layers and possibly the mechanism by which the alkali ions are received into the structure.

APPENDIX 1

Photographs of experimental equipment used in the study

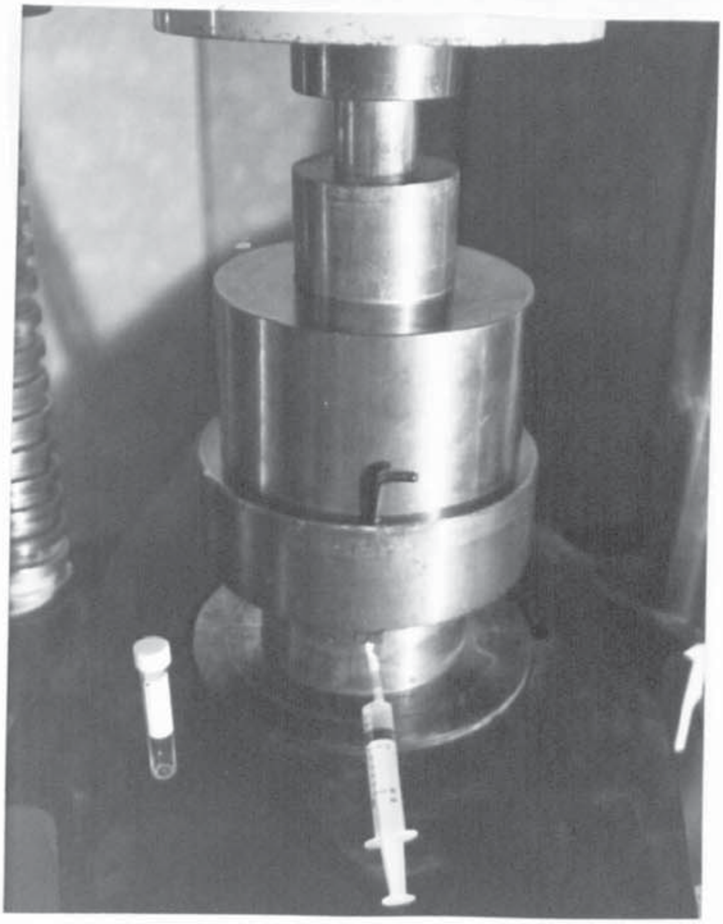
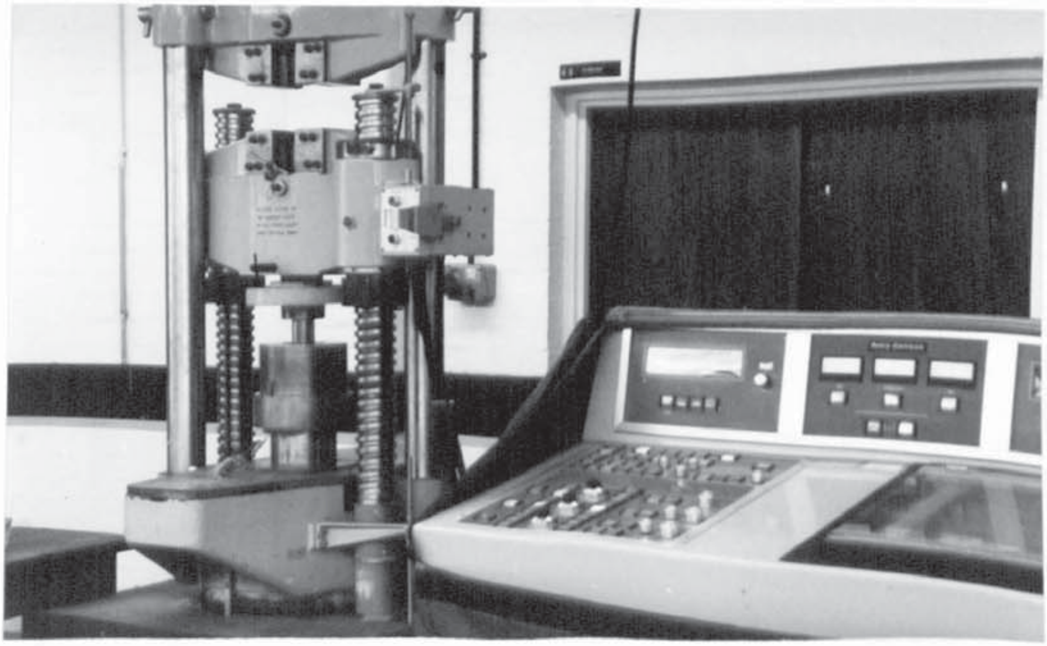


Fig 1.4 Assembled pore solution expression device

Fig 1.5 Expression device in operation



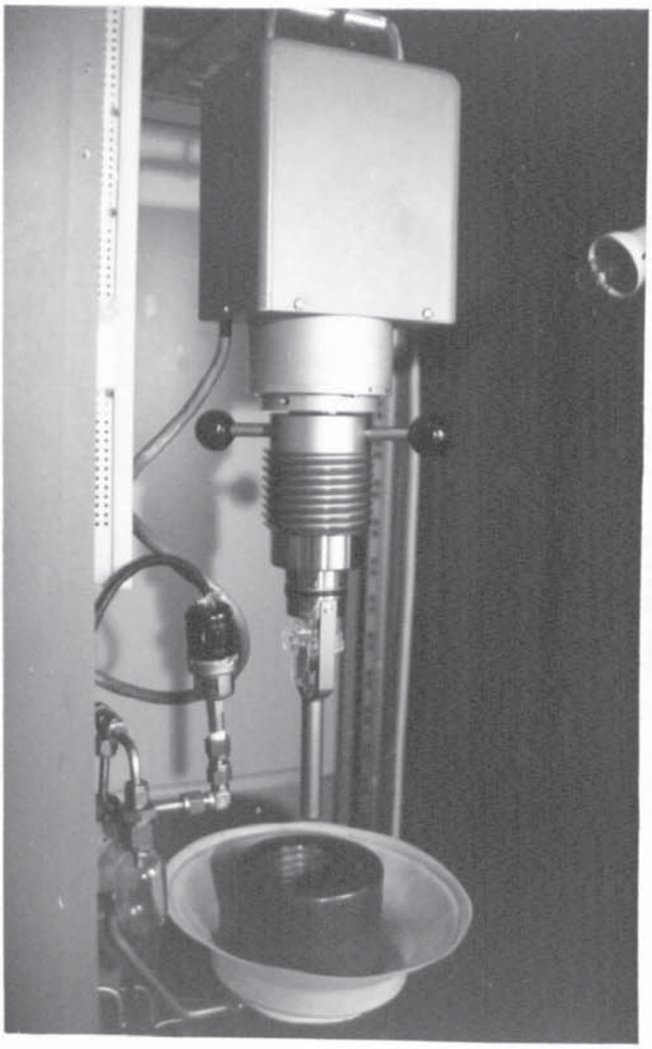
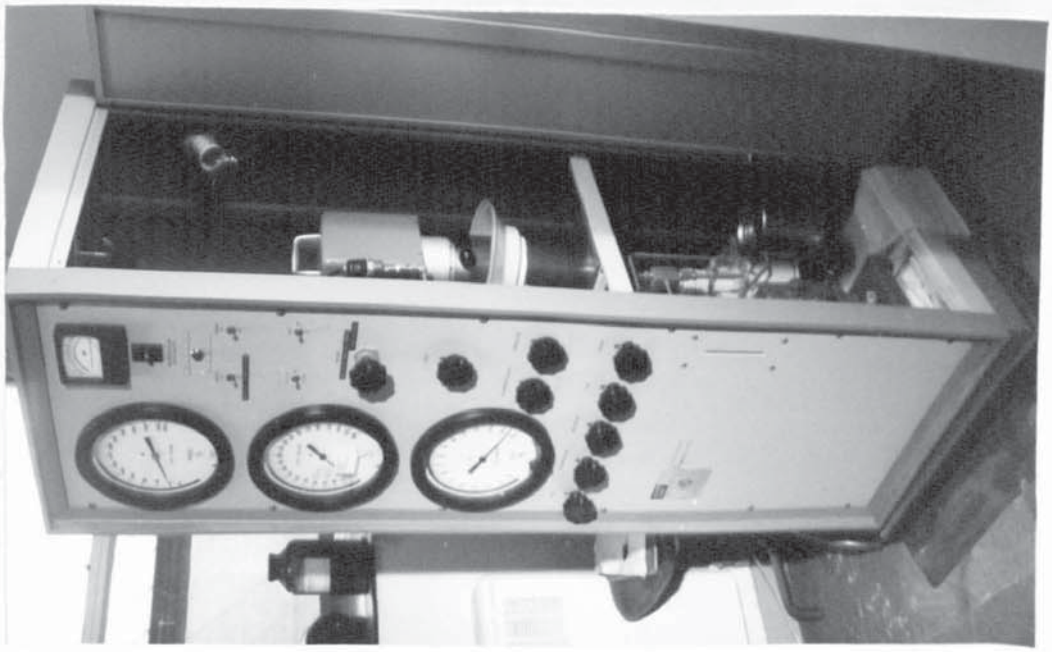


Fig 1.6 Sample ready for pore size distribution determination by Mercury intrusion porosimetry.

Fig 1.7 Micromeritic's Mercury intrusion porosimeter with cell loaded.



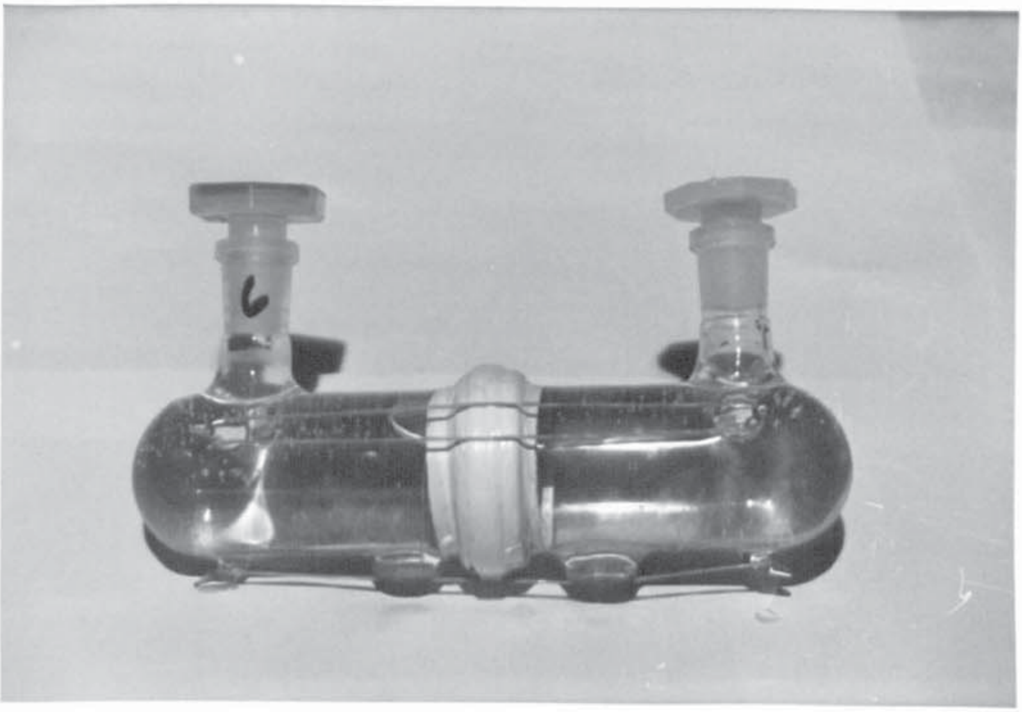
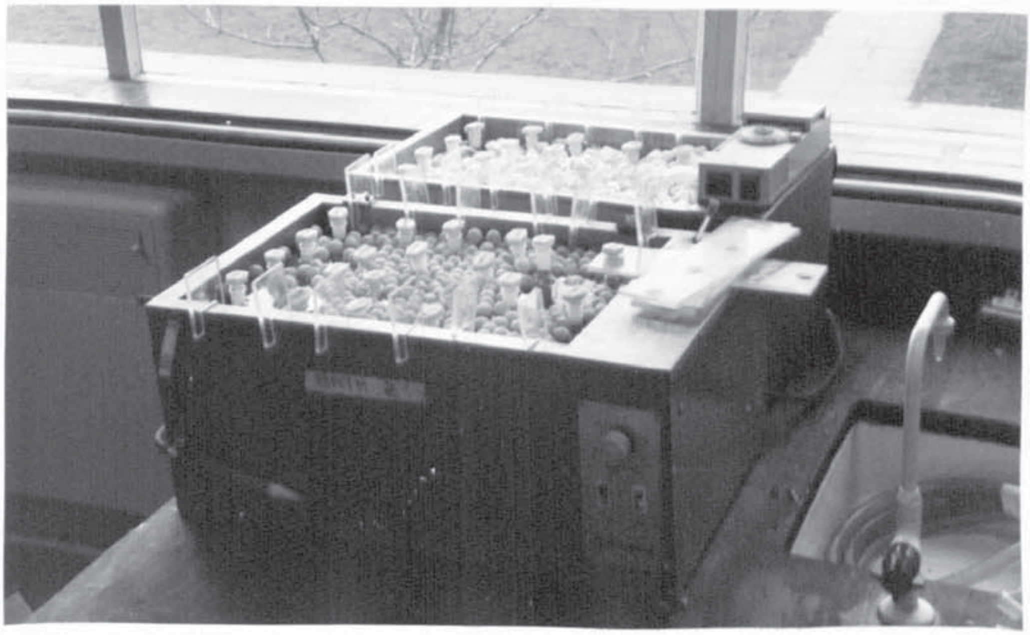


Fig 1.8 Assembled steady state diffusion cell.

Fig 1.9 Diffusion cells kept at constant temperature.



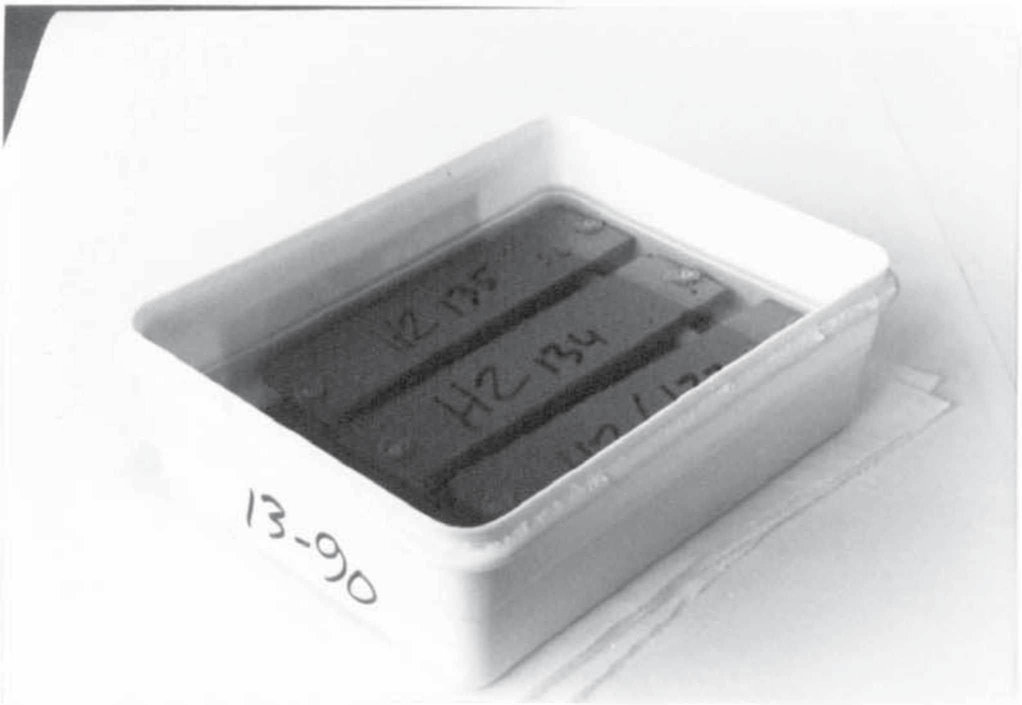
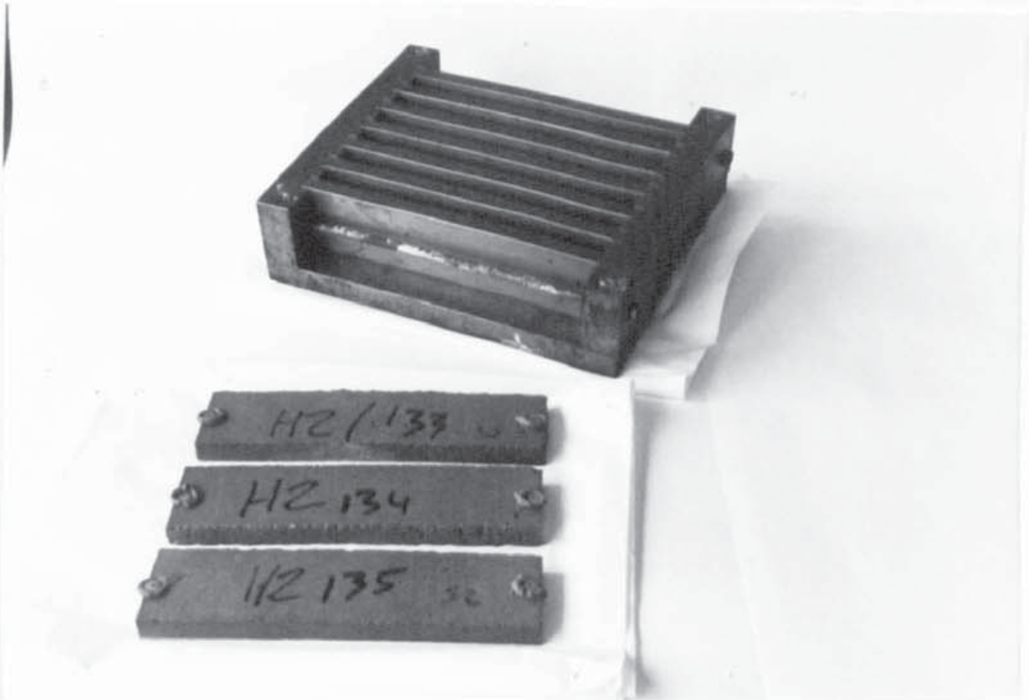


Fig 1.10 Specimens stored under alkaline solutions.

Fig 1.11 Mould and specimens produced for expansion studies.



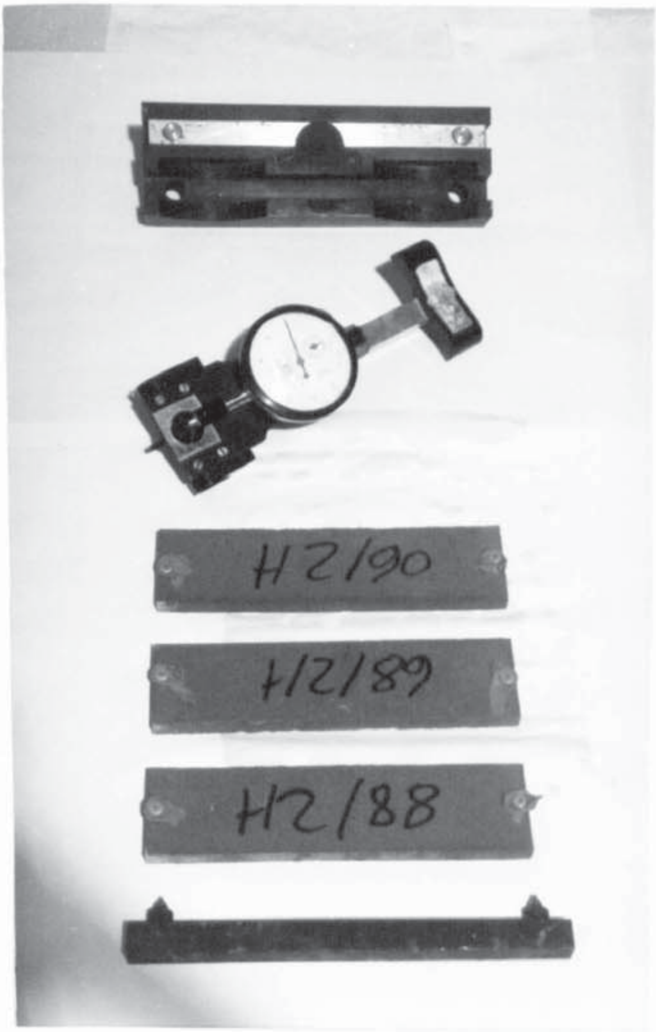
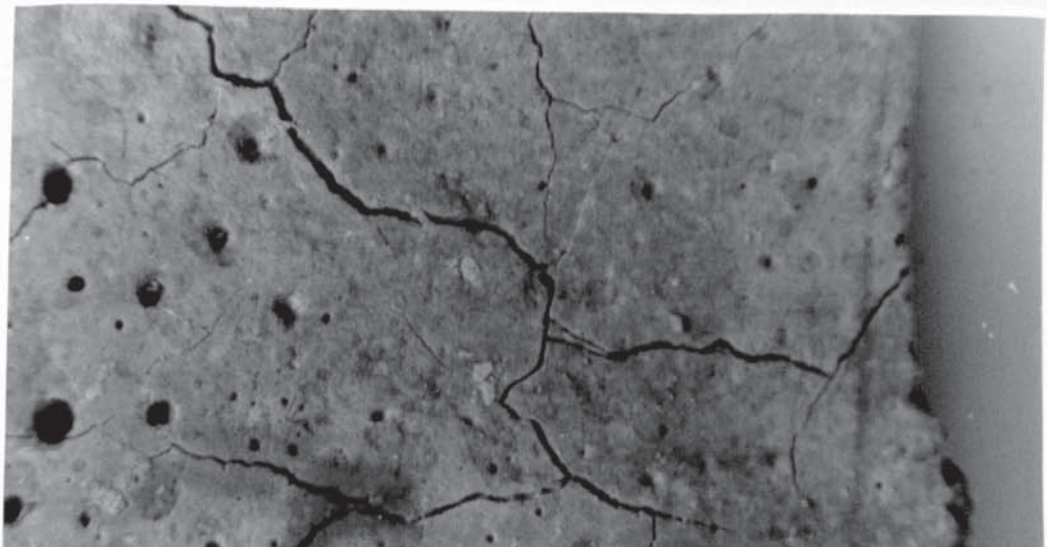


Fig 1.12 Expansion measurement device.

Fig 1.13 Typical ASR cracking pattern observed on specimens.



APPENDIX 2

Chemical Analyses and Physical Properties of materials used in the study

TABLE 2.1 CHEMICAL ANALYSIS OF CEMENTS

Cement	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	LOI	EQ Na_2O
A	67,3	22,3	4,5	0,29	2,5	0,4	0,12	0,16	2,0	0,225
B	63,3	19,5	6,4	3,1	2,8	2,1	0,12	0,84	0,9	0,67
C	60,14	19,91	6,04	2,36	2,79	1,01	0,21	0,99	1,84	0,86
D	64,36	19,63	5,46	3,30	2,83	1,45	0,33	0,96	0,92	0,94
E	64,09	21,2	4,9	1,90	2,50	1,80	0,21	1,30	1,10	1,06

TABLE 2.2 POTENTIAL COMPOUND COMPOSITION

Cement	C_3S	C_2S	C_3A	C_4AF
A	66,7	13,7	11,4	0,90
B	54,0	15,2	11,7	9,4
C	41,6	13,6	12,0	7,2
D	63,3	8,6	9,9	10,0
E	60,3	15,4	9,8	5,8

TABLE 2.3 CHEMICAL ANALYSIS OF PULVERISED FUEL ASHES USED IN STUDY

PFA	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	P_2O_5	TiO_2	Minor	LOI	Na_2O	K_2O	$EqNa_2O$
1	1,85	51,13	28,22	8,13	0,79	1,32	-	1,20	-	2,81	0,96	3,71	3,40
2	1,37	51,09	25,81	8,84	0,73	1,37	0,23	0,96	0,32	4,18	1,36	3,05	3,37
3	1,17	51,19	24,45	9,14	0,63	1,42	0,20	0,90	0,33	4,93	1,25	2,97	3,20
4	2,71	49,29	33,52	5,48	0,35	1,27	0,87	1,30	0,51	2,01	0,28	1,16	1,04
5	2,71	48,14	31,18	5,63	0,32	1,25	0,85	1,18	0,50	6,89	0,25	1,10	0,97

%

TABLE 2.4 SUMMARY OF PROPERTIES OF PULVERISED ASHES

PFA	45μm Residue (12,5%)	LOI (7% max)	MgO (4% max)	SO_3 (2,5% Max)	Water Reqt. (95% max)	Pozzolanic Index (85% min)	BS4550 Ranking	Eq. Na_2O%	Description
1	5,4	2,81	1,32	0,79	-	-	-	3,40	HA,F
2	4,4	4,2	1,37	0,73	89	131	1	3,37	HA,F
3	13,8*	4,9	1,42	0,63	89	103	2	3,20	HA,C
4	4,6	2,0	1,27	0,35	87	112	3	1,04	LA,F
5	16,4*	6,9	1,25	0,32	96*	90	4	0,97	LA,C

* Failure to comply with B.S.3892 Part 1.

CHEMICAL ANALYSIS OF BLAST FURNACE SLAGS USED IN STUDY

TABLE 2.5

SLAG	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	S^{2-}	TiO_2	Minor	Na_2O	K_2C	Eq Na_2O
1 Granulated	39,39	36,67	11,48	0,70	1,29	7,77	NIL	0,56	0,96	0,43	0,82	0,969
2 Pelletised	36,50	39,99	7,52	2,04	0,15	9,84	1,40	0,44	1,79	0,36	0,58	0,742
3 Granulated	42,32	36,03	9,35	0,91	0,9	7,39	NIL	0,56	0,73	0,29	0,47	0,599

%

SIEVE ANALYSIS

TABLE 2.6 — Cheddar Limestone 20-10 mm.

AGGREGATE SIZE		% RETAINED (BY WEIGHT)
+ 20 mm		0
- 20 mm	+ 14 mm.	57.37
- 14 mm	+ 10 mm.	41.89
- 10 mm	+ 6.3 mm.	0.59
- 6.3 mm		0

TABLE 2.7 — Cheddar Limestone 5 mm. down

+ 5 mm		0.22
- 5 mm	+ 3.35 mm	17.36
- 3.35 mm	+ 2.36 mm	22.03
- 2.36 mm	+ 1.18 mm	25.71
- 1.18 mm	+ 600 μm	13.06
- 600 μm	+ 300 μm	7.98
- 300 μm		13.57

TABLE 2.8 — Beltane Opal 300-150 μm

+ 300 μm		0
- 300 μm	+ 150 μm	100
- 150 μm		0

TABLE 2.9.1 TYPICAL CHEMICAL COMPOSITION OF BELTANE OPAL

BELTANE OPAL	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	Eq.Na_2O	LOI
%	91,38	2,10	0,13	0,10	0,20	0,10	0,23	5,6 as water 0,3 as CO_2

Gutteridge and Hobbs (79)

TABLE 2.9.2

Barneyback (39)

BELTANE OPAL	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	Eq.Na_2O	LOI
%	87,96	3,91	0,29	0,28	0,26	0,14	0,31	6,54

APPENDIX 3

Calculation of mix design for mortar prisms used in Chapter 3

1. The cement required per 6 specimens — 240 grms
2. Therefore, using A/C 2.75, the total aggregate required — 660 grms
3. Beltane opal substituted at the level of 12 grms/100

   $$\frac{660}{100} \times 12$$ 79.2 grms

4. 14 percent of the limestone aggregate passed the 300 μm sieve (see table 2.6). Therefore, the quantity of sub 300μm aggregate present.

   $$660 \times \frac{14}{100}$$ 92.4 grms

5. As Beltane is in the grading size of sub 300μm account must be taken of this.

   $$\begin{array}{r} 92.40 \\ \underline{-79.20} \end{array}$$ 13.2 grms

6. The remaining aggregate can now be made up with the -5mm + 300μm graded limestone.

   $$\begin{array}{r} 660 \\ \underline{92.40} \end{array}$$ 567.6 grms

To Summarise

Cement A	240 grms
Aggregate (-5mm + 300μm)	567.6 grms
(Beltane Opal)	79.2 grms
(-300 μm)	13.2 grms
Water (0.55)	132.0 grms

APPENDIX 3

Expansion data - extracted from specimens subjected to alkali solutions

Table 3.4 Plain cement specimens

Concentration	To (hours)	Ultimate expansion (%)	Expansion/time relationship
13.30	888	1.99	E = 0.00095. T-0.599
13.45	552	2.06	E = 3.438 log T-9.758
13.60	240	2.22	E = 3.131 log T-8.524
13.75	120	2.20	E = 2.232 log T-5.398
13.90	72	2.14	E = 2.173 log T-5.182

Table 3.5 20% pfa 2

13.30	4680	0.04	E = 0*
13.45	1344	0.62	E = 0.0001. T-0.125
13.60	768	0.89	E = 0.0151. T-0.357
13.75	456	1.26	E = 1.467 log T-4.234
13.90	384	1.31	E = 1.342 log T-3.830

Table 3.6 20% pfa 3

13.30	3168	0.05	E = 0*
13.45	1176	2.40	E = 0.00121. T-0.163
13.60	480	2.44	E = 0.0518. T-1.243
13.75	288	1.57	E = 1.134 log T-2.660
13.90	216	2.07	E = 2.159 log T-5.850

Table 3.7 20% pfa 4

13.30	4392	0.03	E = 0*
13.45	1680	0.57	E = 0.000121. T-0.163
13.60	480	0.82	E = 0.015. T-0.314
13.75	456	0.92	E = 0.759 log T-1.982
13.90	384	1.00	E = 0.960 log T-2.513

* Expansion too small for accurate assessment

Table 3.8 20% pfa 5

Concentration	To (hours)	Ultimate expansion (%)	Expansion/time relationship
13.30	6720	0.02	E = 0*
13.45	2016	0.56	E = 0.000126 T-0.242
13.60	624	1.02	E = 0.018 T-0.423
13.75	456	1.06	E = 1.045 log T-2.903
13.90	360	1.22	E = 1.013 log T-2.592

Table 3.9 40% pfa 2

13.30	4386	0.04	E = 0*
13.45	1848	0.11	E = 0.00002 T-0.013
13.60	1008	0.35	E = 0.00005 T-0.013
13.75	744	0.59	E = 0.003 T-0.051
13.90	744	0.47	E = 0.0081 T-0.183

Table 3.10 40% pfa 3

13.30	3864	0.05	E = 0*
13.45	1512	0.22	E = 0.00004 T-0.022
13.60	624	0.60	E = 0.01 T-0.206
13.75	432	0.71	E = 0.254 log T-0.742
13.90	384	0.64	E = 0.0103 T-0.207

Table 3.11 40% pfa 4

13.30	6720	0.03	E = 0*
13.45	6000	0.04	E = 0.00002 T-0.079
13.60	2016	0.12	E = 0.00002 T-0.0154
13.75	1176	0.30	E = 0.01 T-0.038
13.90	624	0.43	E = 0.008 T-0.205

Table 3.12 40% pfa 5

13.30	6720	0.01	E = 0*
13.45	5424	0.03	E = 0.00001 T-0.051
13.60	2016	0.23	E = 0.005 T-0.201
13.75	1152	0.51	E = 0.009 T-0.171
13.90	480	0.54	E = 0.009 T-0.194

Table 3.13 40% slag 1

Concentration	To (hours)	Ultimate expansion (%)	Expansion/time relationship
13.30	6720	0.02	E = 0*
13.45	2016	0.23	E = 0.00004 T-0.03
13.60	1392	0.61	E = 0.896 log T-2.821
13.75	672	1.32	E = 0.0002 T-0.0096
13.90	240	0.25	E = 1.353 log T-3.786

Table 3.14 40% slag 2

13.30	5328	0.03	E = 0*
13.45	2928	0.55	E = 0.00014 T-0.372
13.60	1200	1.07	E = 1.962 log T-6.440
13.75	720	1.77	E = 0.0003 log T-0.262
13.90	552	1.44	E = 1.865 log T-5.519

Table 3.15 40% slag 3

13.30	5328	0.03	E = 0*
13.45	2424	0.62	E = 0.00014 T-0.303
13.60	1250	1.46	E = 2.044 log T-6.364
13.75	288	1.69	E = 2.05 log T-6.135
13.90	192	1.35	E = 0.00006 T-0.08

Table 3.16 60% slag 1

13.30	6720	0.02	E = 0*
13.45	4080	0.04	E = 0*
13.60	3408	0.04	E = 0*
13.75	2424	0.05	E = 0.000006 T+0.008
13.90	1560	0.25	E = 0.0002 T+0.009

Table 3.17 60% slag 2

13.30	6720	0.02	E = 0*
13.45	6720	0.02	E = 0*
13.60	5328	0.03	E = 0*
13.75	3624	0.07	E = 0.000013 T-0.019
13.90	2280	0.31	E = 0.00006 T-0.112

Table 3.18 60% slag 3

Concentration	To (hours)	Ultimate expansion (%)	Expansion/time relationship
13.30	6720	0.03	E = 0*
13.45	2928	0.04	E = 0*
13.60	2424	0.05	E = 0*
13.75	2024	0.26	E = 0.639 log T-2.181
13.90	1560	0.54	E = 1.056 log T-3.49

* Expansion too small for accurate assessment

Table 3.19 Mean values plain cement mortars

	Ultimate Exp^n (%)	Exp^n @ 2688 Hours (%)	To (hours)	To factor	permeability factor ε_o
13.30	1.99	1.99	888		
13.45	2.06	2.06	552		
13.60	2.22	2.22	240		
13.75	2.20	2.20	120		
13.90	2.14	2.14	72		

Table 3.20 Mean values specimens with 20% pfa

13.30	0.04	0	4740	5.34	-
13.45	0.58*	0.14	1554	2.82	7.81
13.60	0.91*	0.47*	588	2.45	4.05
13.75	1.20	0.70*	414	3.45	2.78
13.90	1.40	0.81*	336	4.67	2.66

Table 3.21 Mean values specimens with 40% pfa

13.30	0.03	0	5418	6.10	-
13.45	0.10	0.03	3696	6.70	-
13.60	0.33	0.13	1416	5.90	8.87
13.75	0.53	0.28	876	7.30	5.54
13.90	0.52	0.26	558	7.75	7.52

Table 3.22 Values specimens with 40% slag

13.30	0.03	0	5792	6.52	-
13.45	0.47	0.05	2456	4.45	4.47
13.60	1.05	0.40	1281	5.34	3.19
13.75	1.59	0.69	560	4.67	2.64
13.90	1.40+	0.86	328	4.56	2.52

Table 3.23 Mean values specimens with 60% slag

13.30	0.02	0	6720	7.57	-
13.45	0.03	0	4576	8.29	-
13.60	0.04	0	3720	15.50	-
13.75	0.13	0	2691	22.43	-
13.90	0.37	0.09	1800	25.00	9.05

To figures for plain specimens are estimated

* Pfa 3 not included   + Slag 1 not included

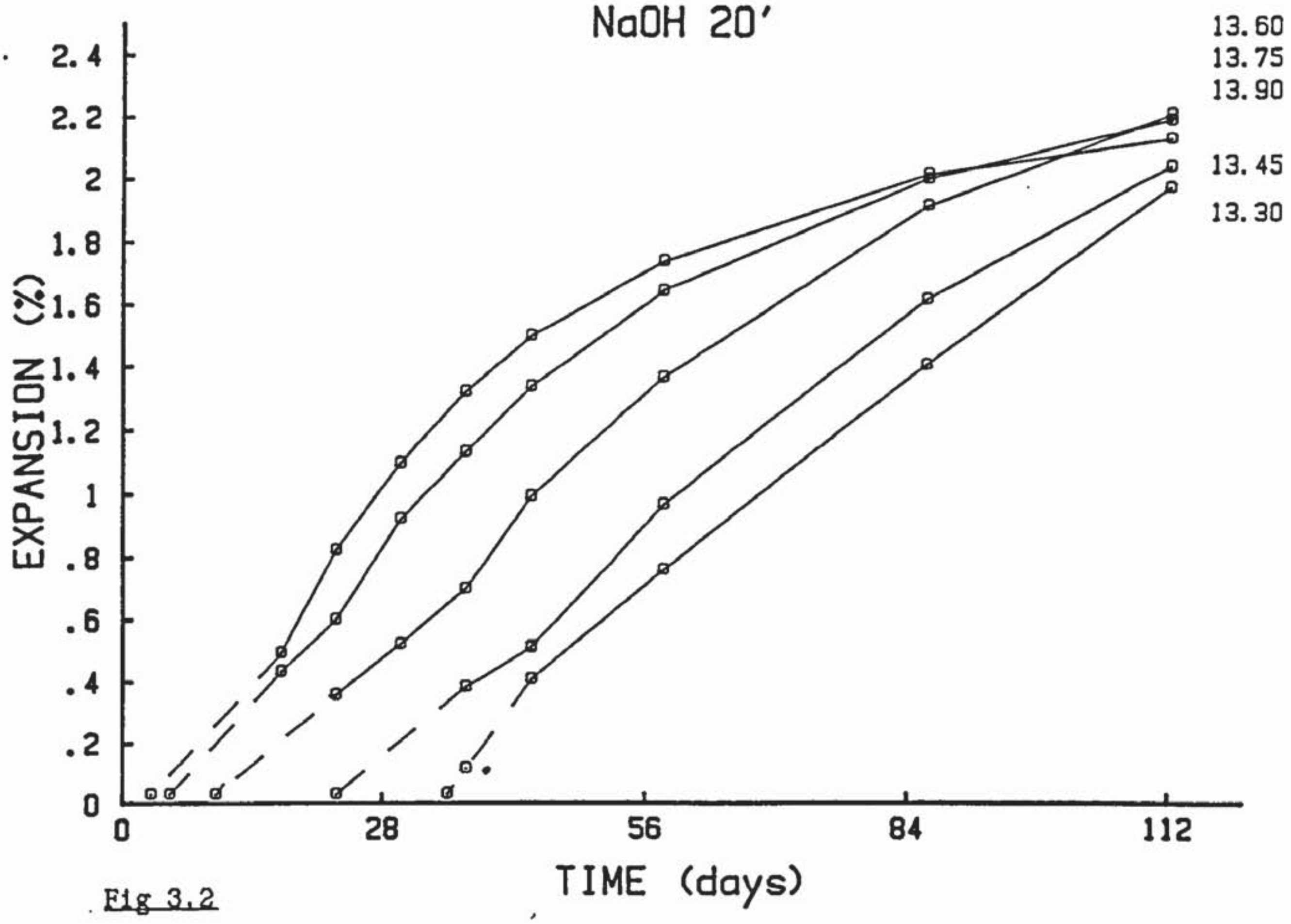
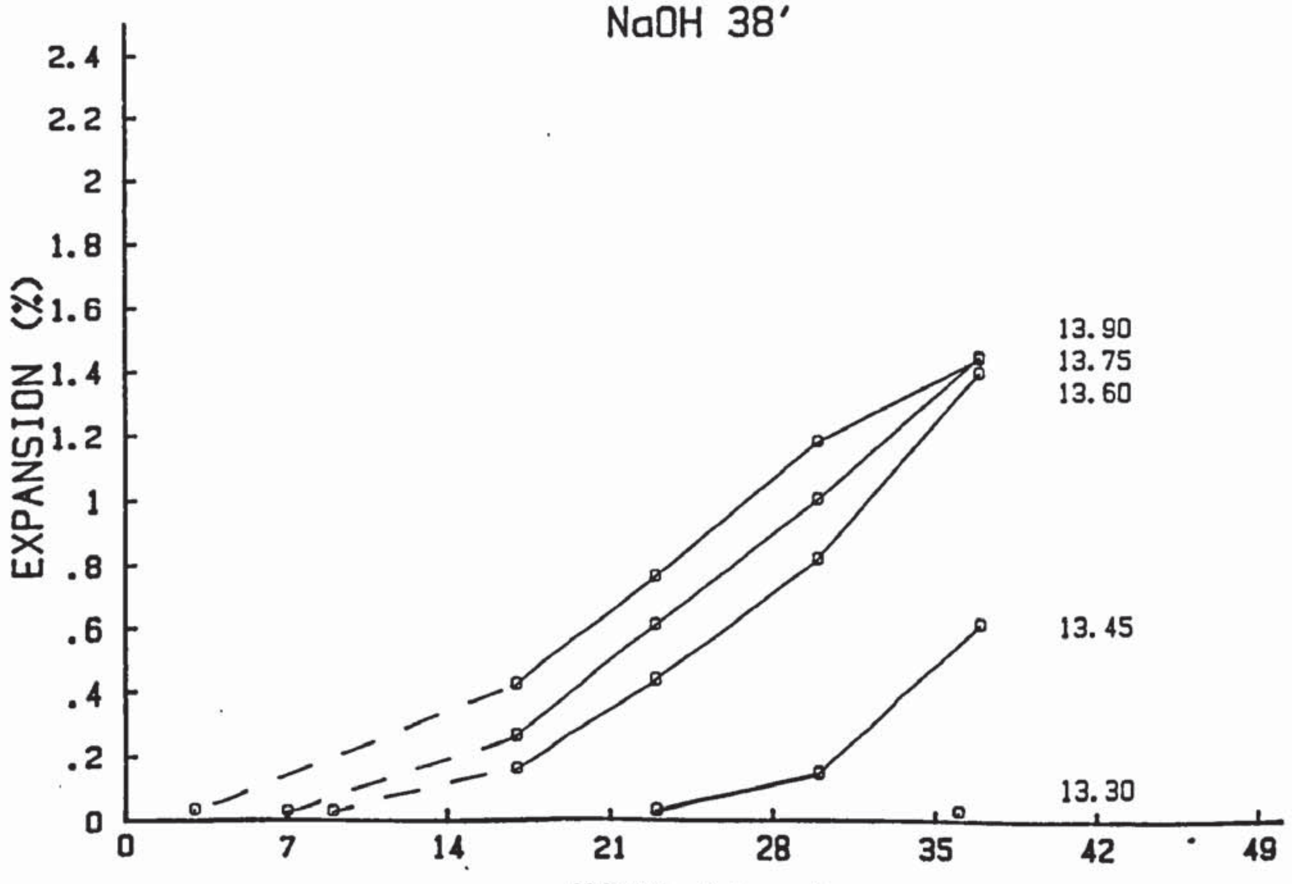


Fig 3.2

% Expansion as a function of time

Fig 3.3



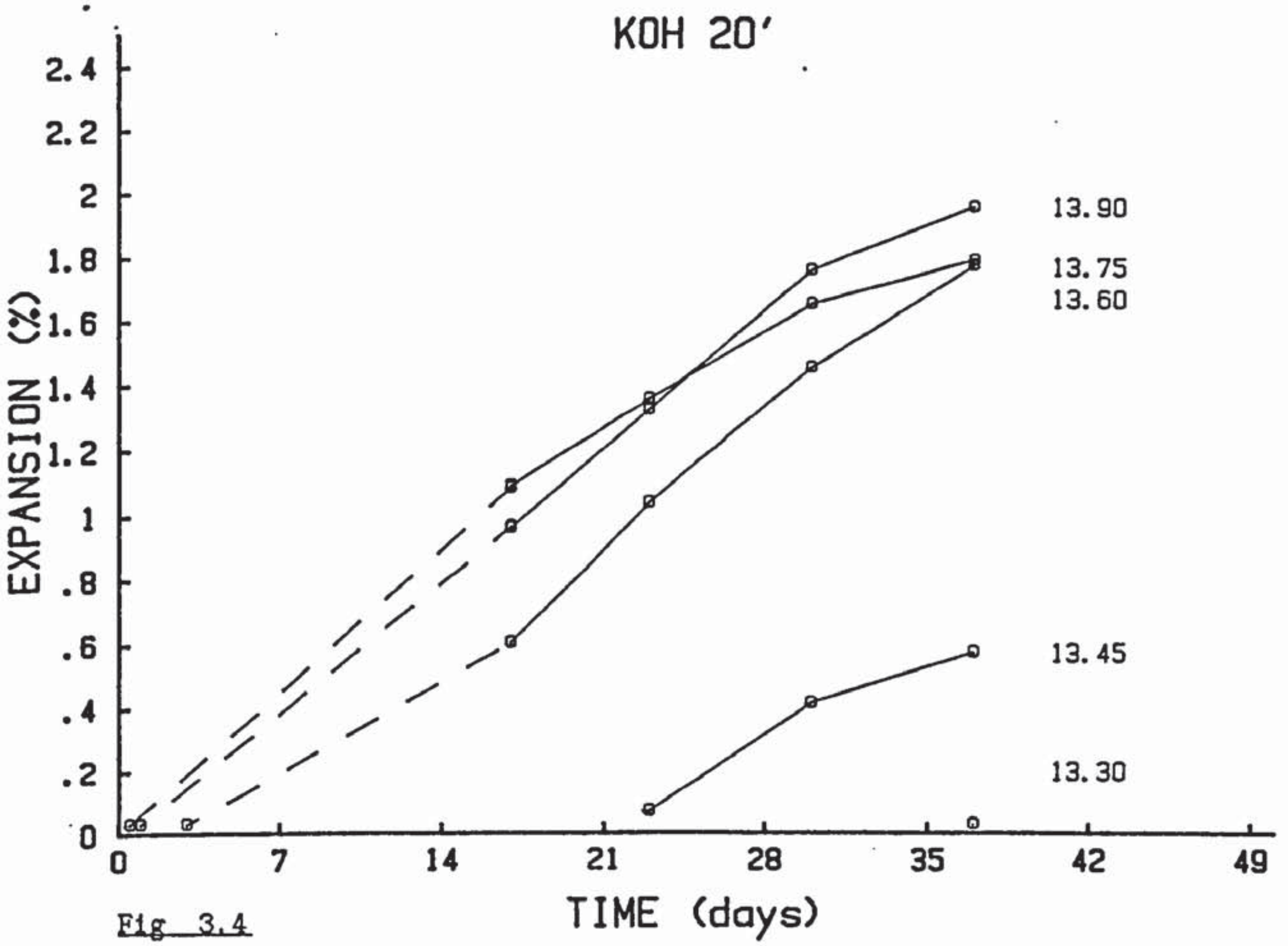
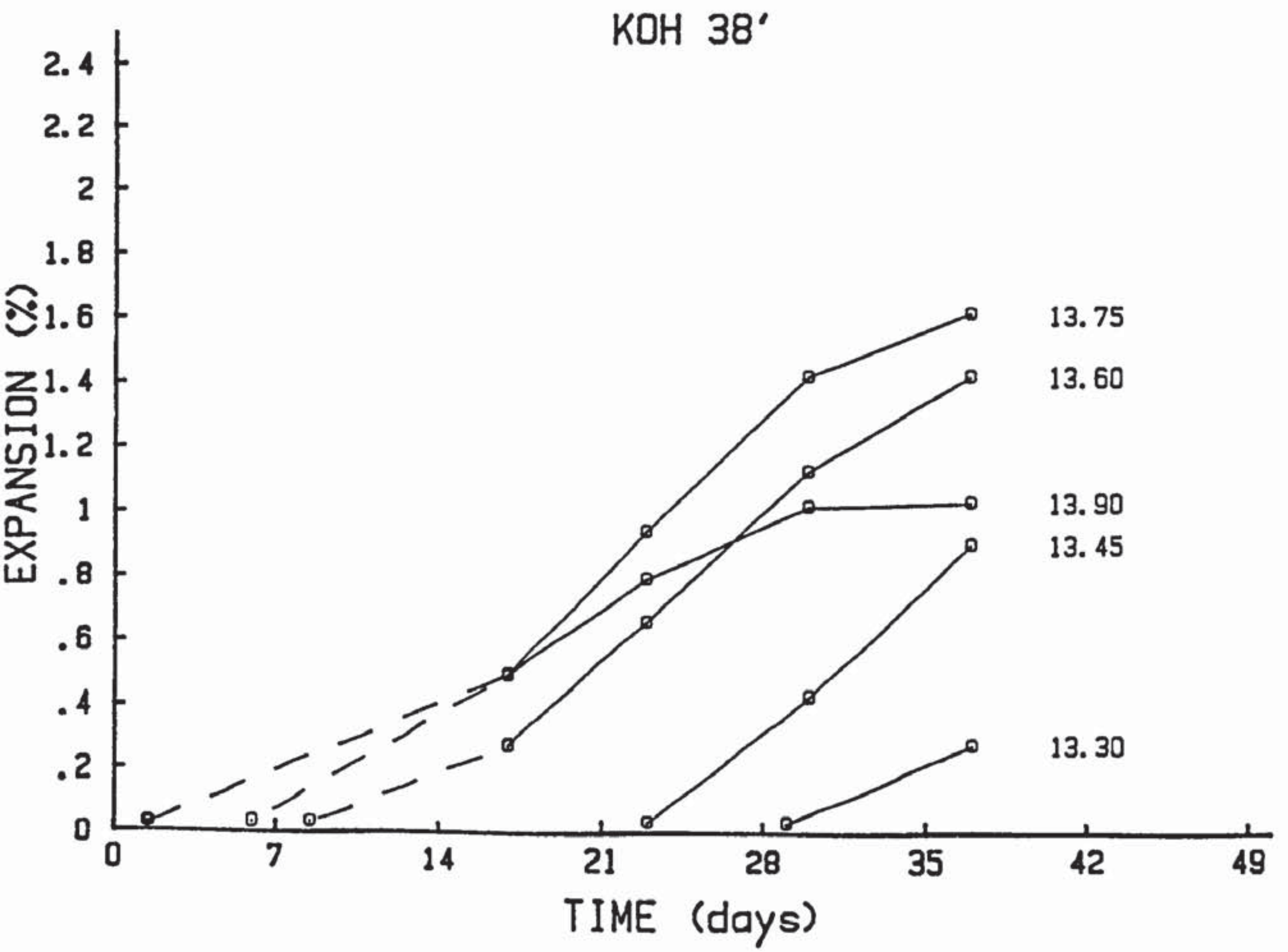


Fig 3.4

% Expansion as a function of time

Fig 3.5



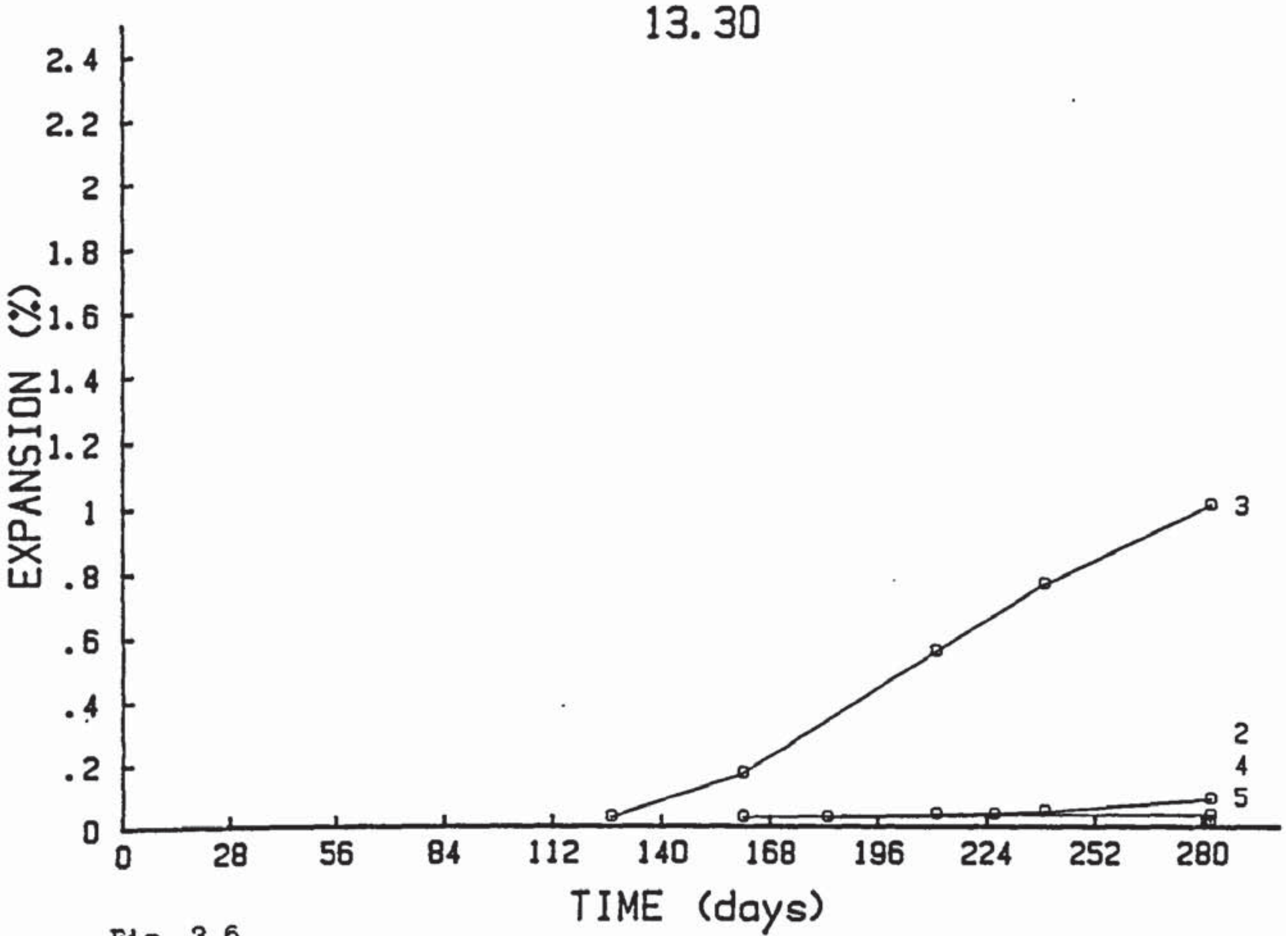


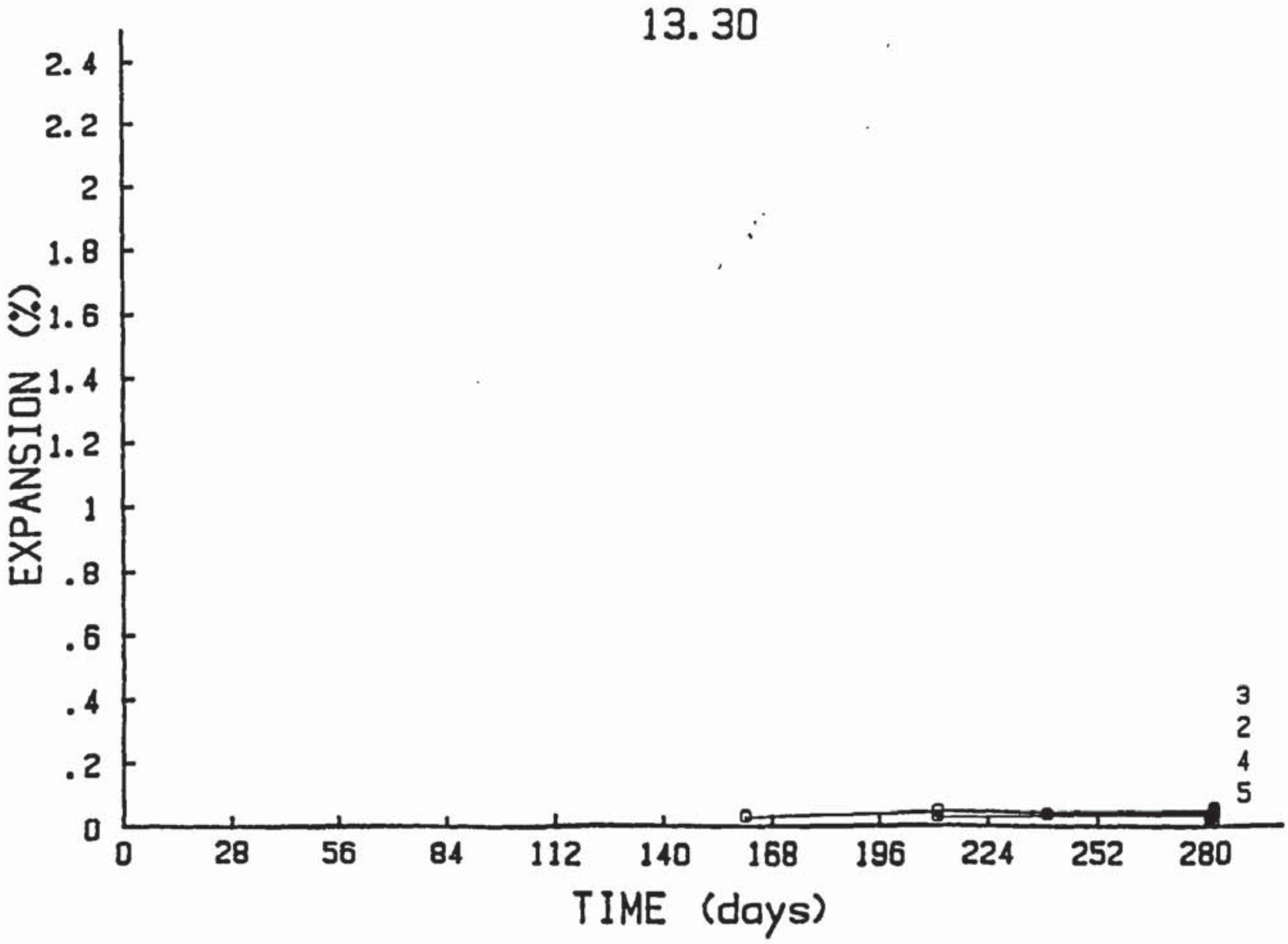
Fig 3.6

20% Pfa

Expansion (%) vs time ash blended cements stored under NaOH at 20°C

40% Pfa

Fig 3.7



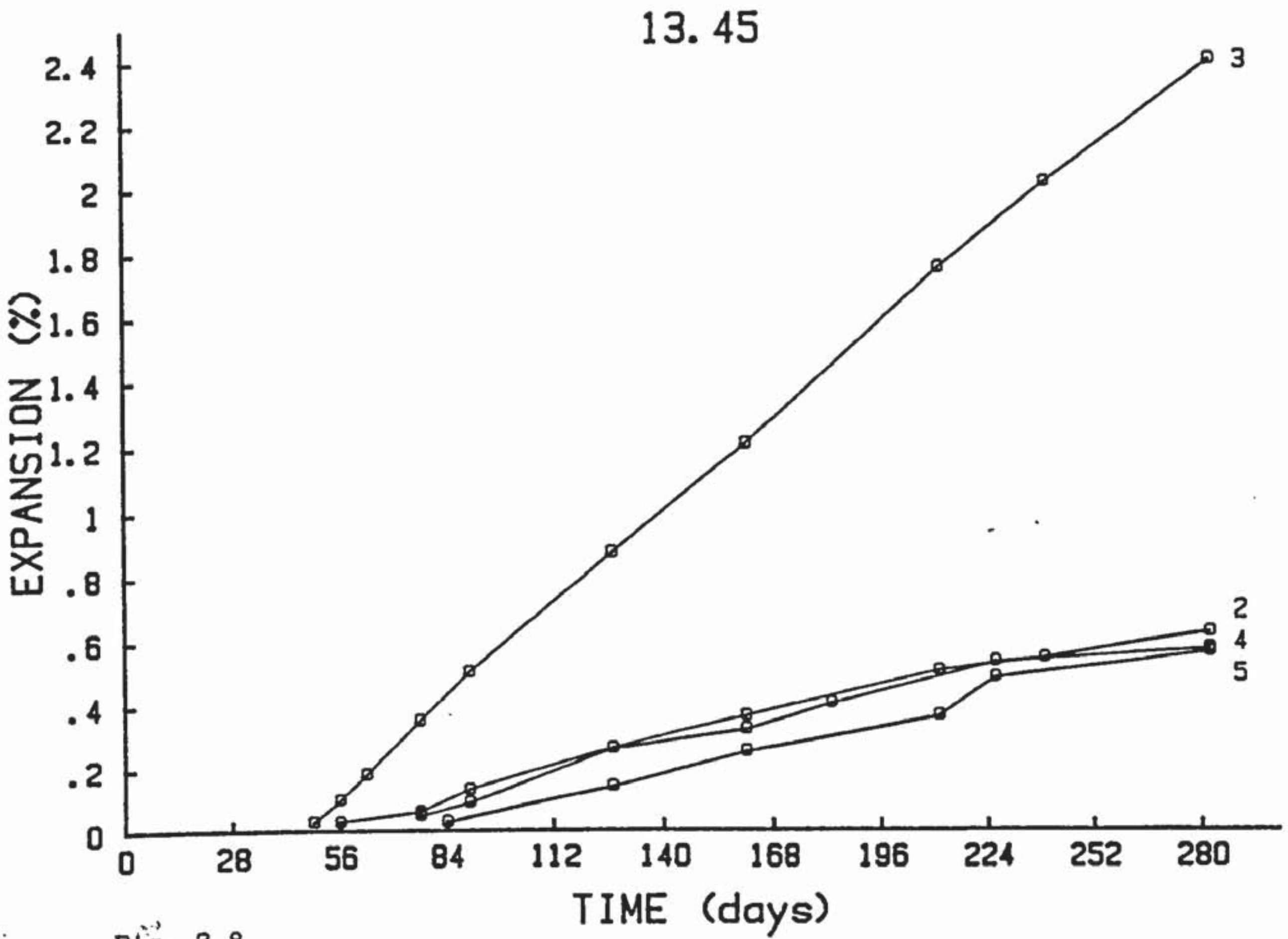


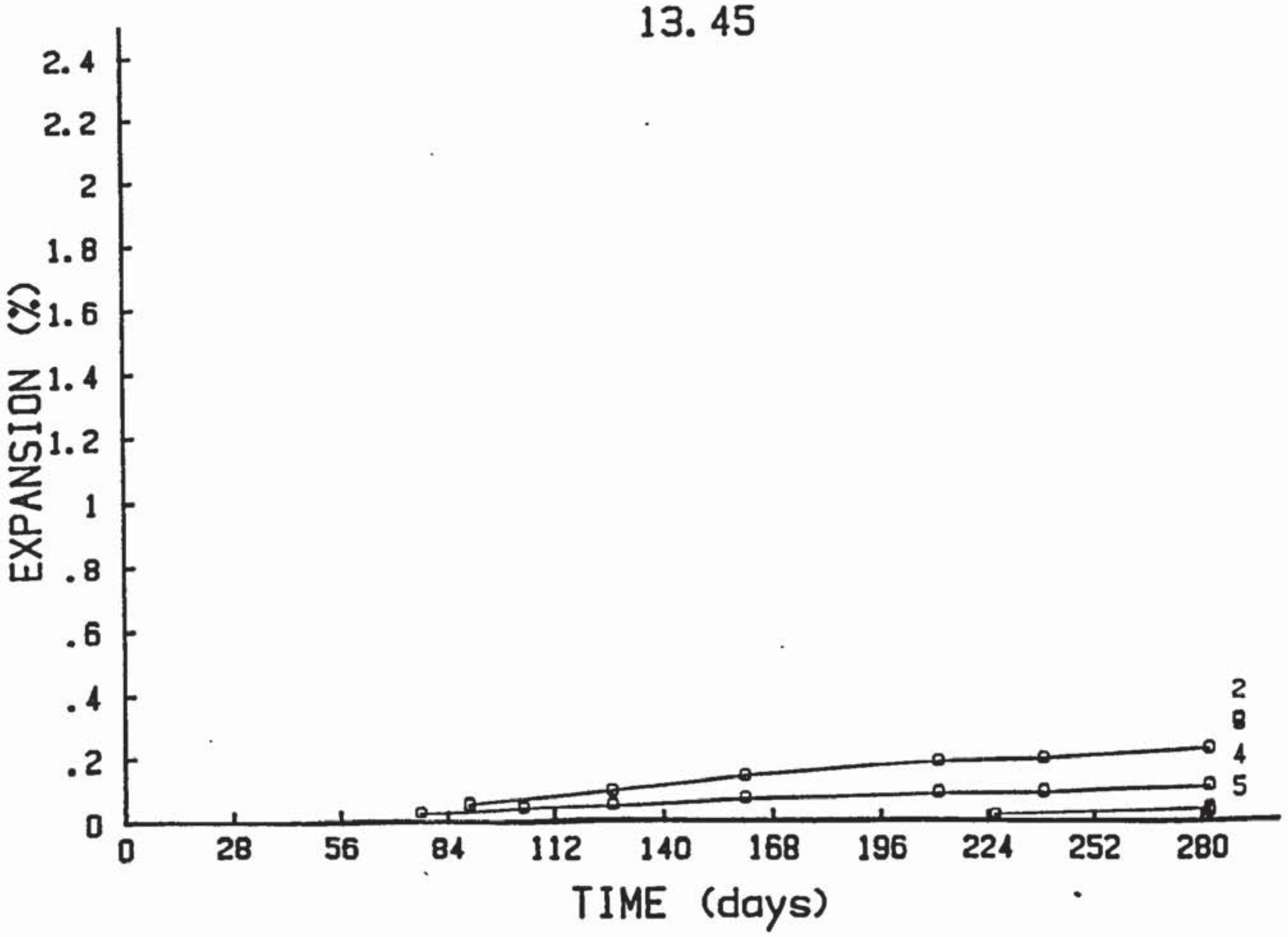
Fig 3.8

20% Pfa

Expansion (%) Vs time

40% Pfa

Fig 3.9



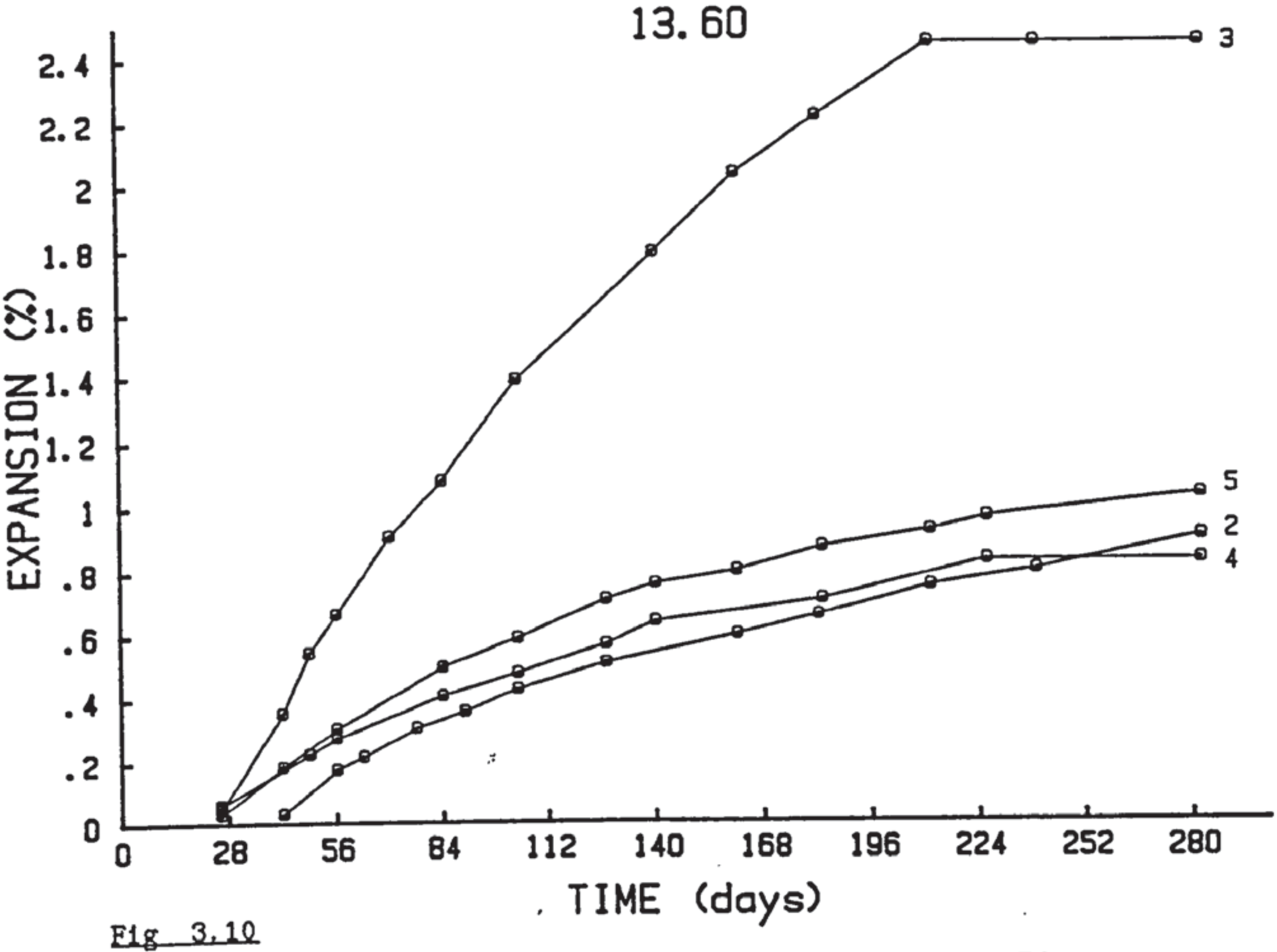


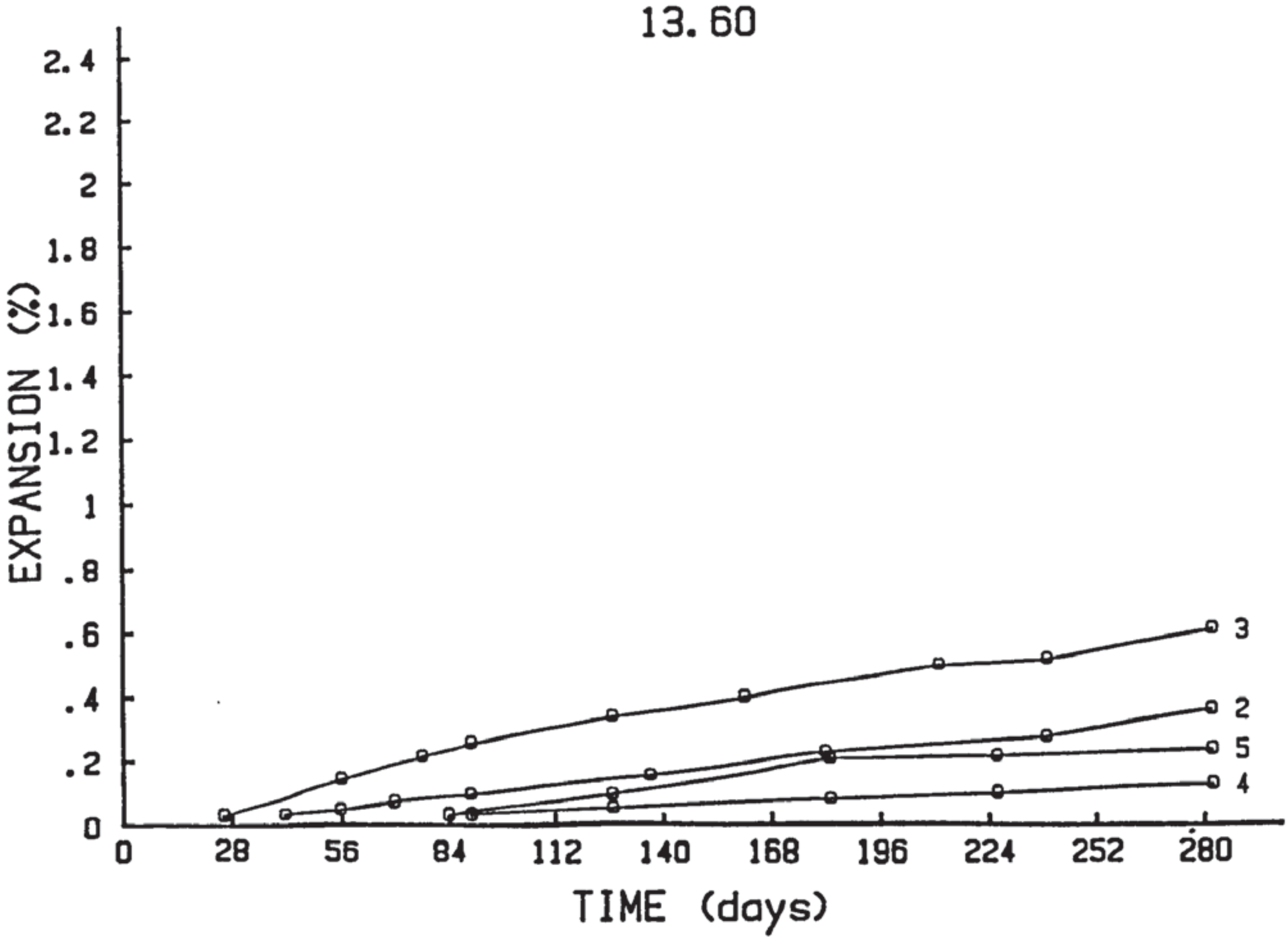
Fig 3.10

20% Pfa

Expansion (%) Vs time

40% Pfa

Fig 3.11



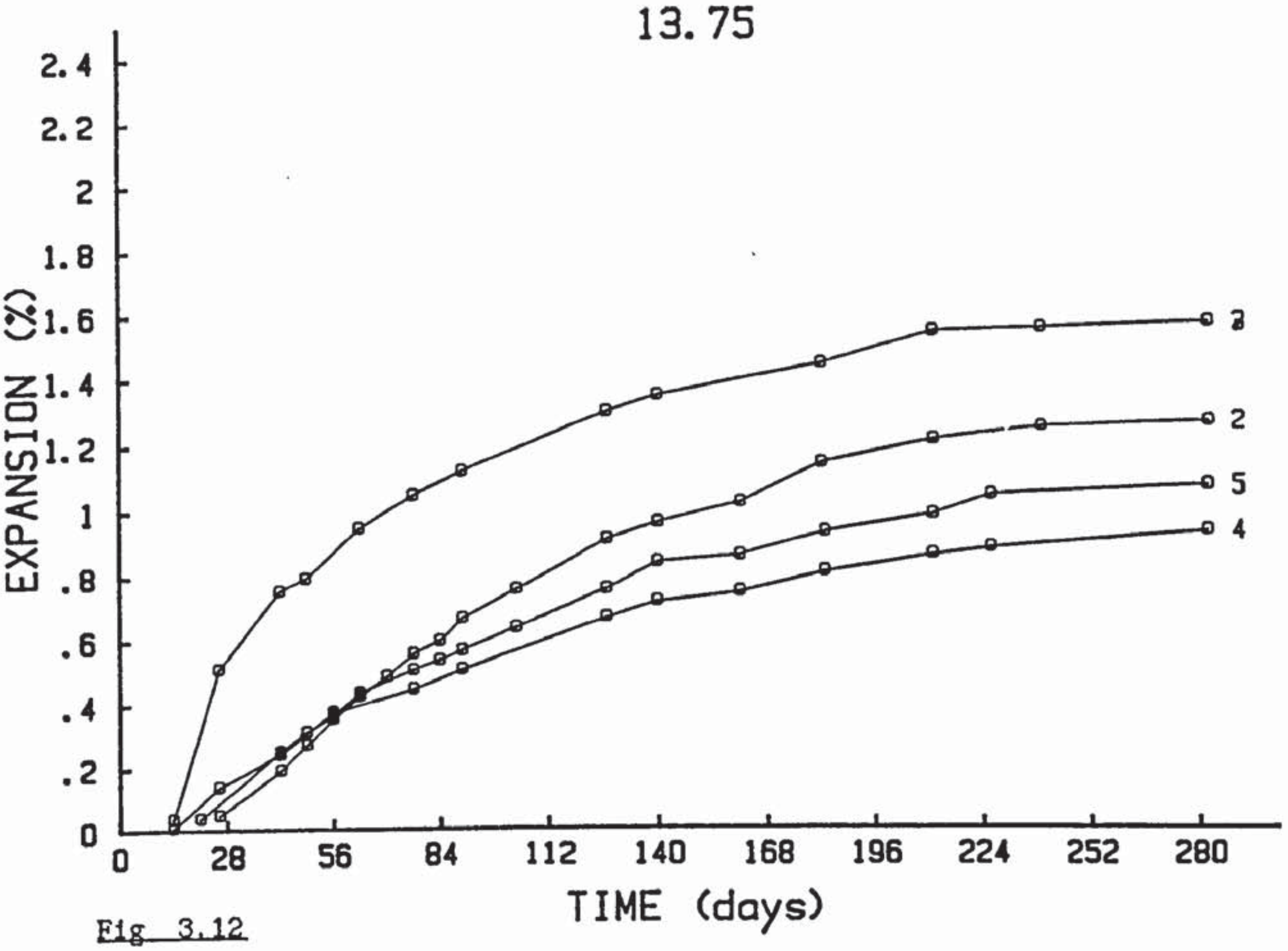


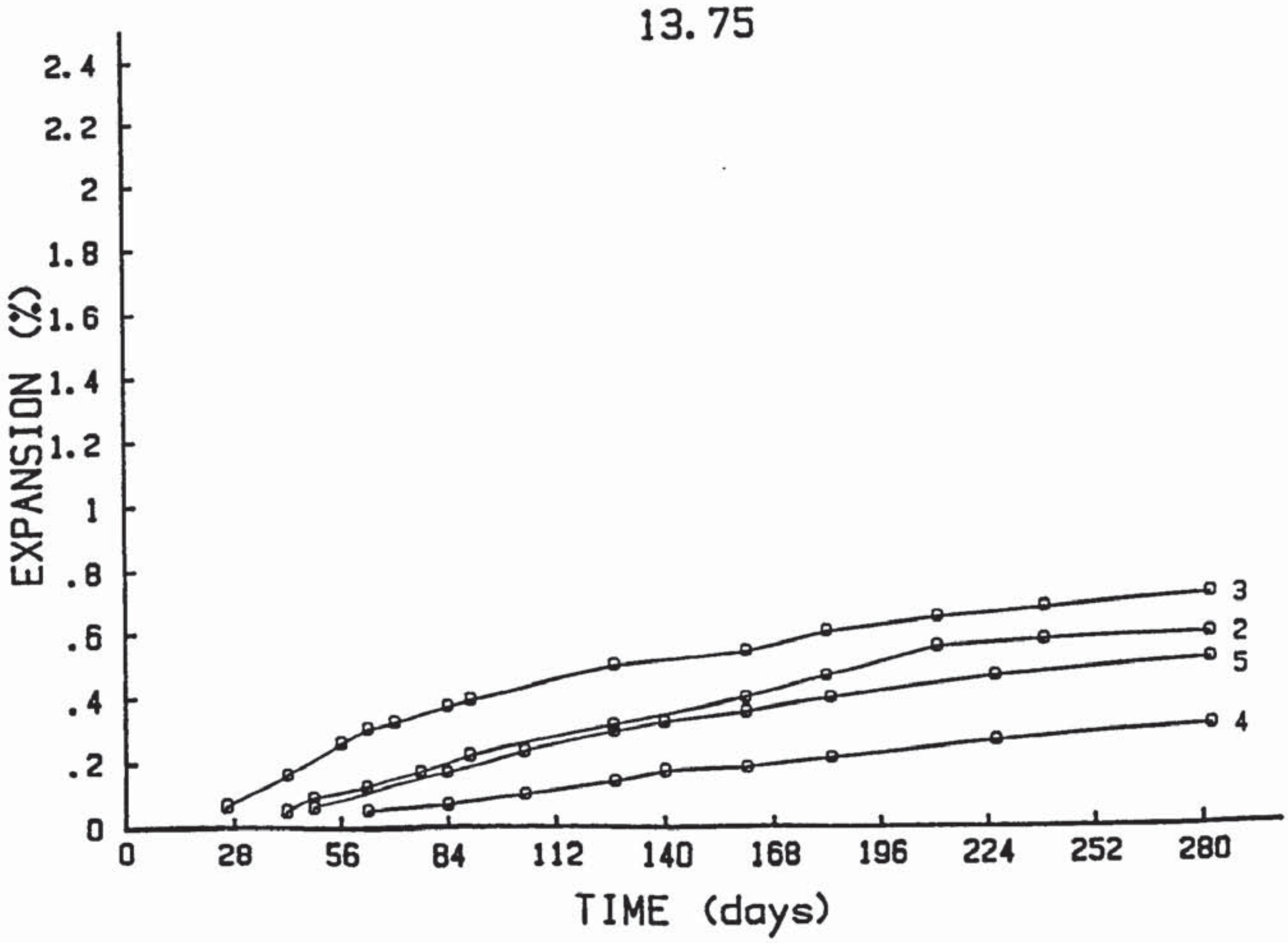
Fig 3.12

20% Pfa

Expansion (%) Vs time

40% Pfa

Fig 3.13



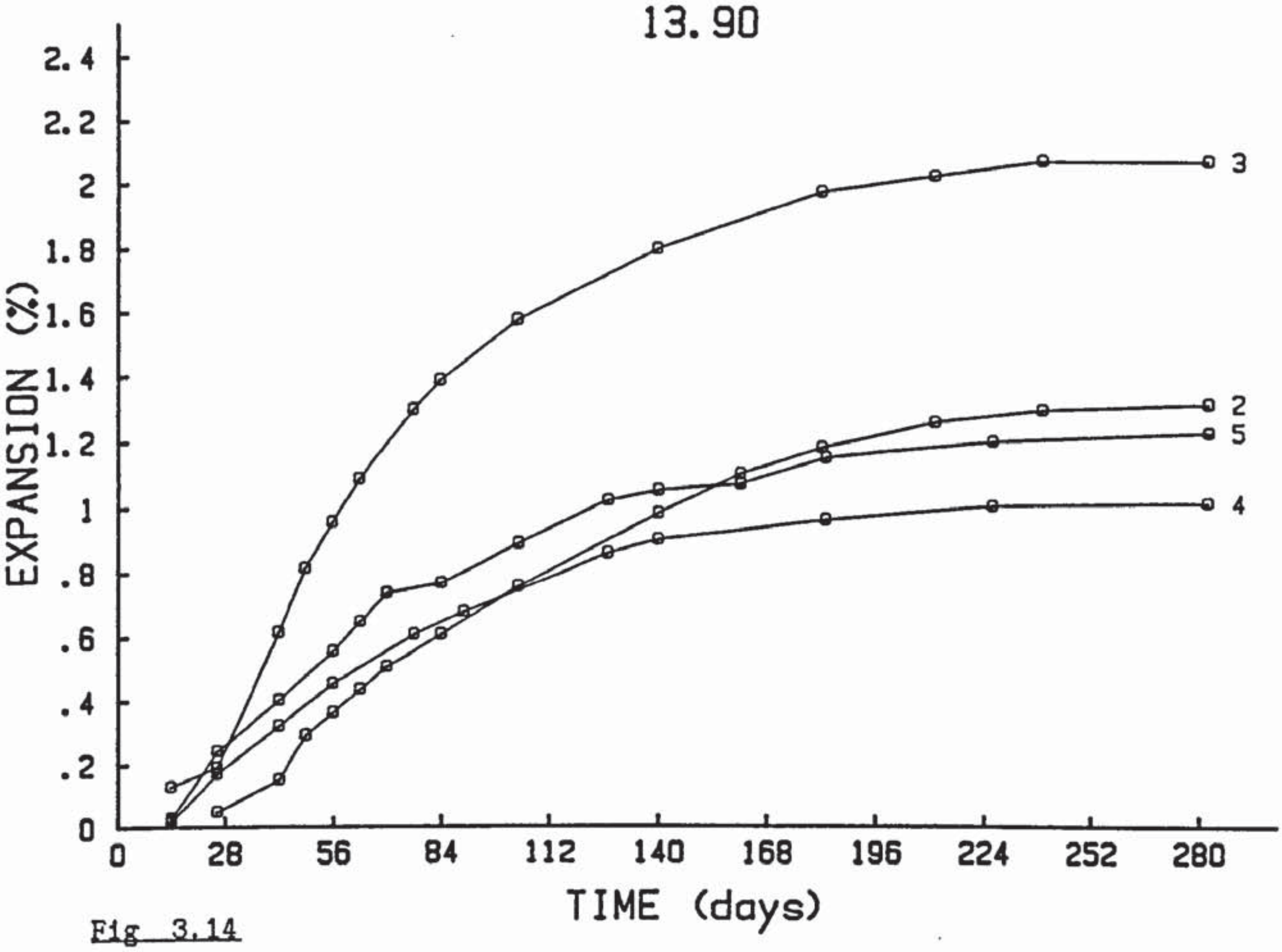


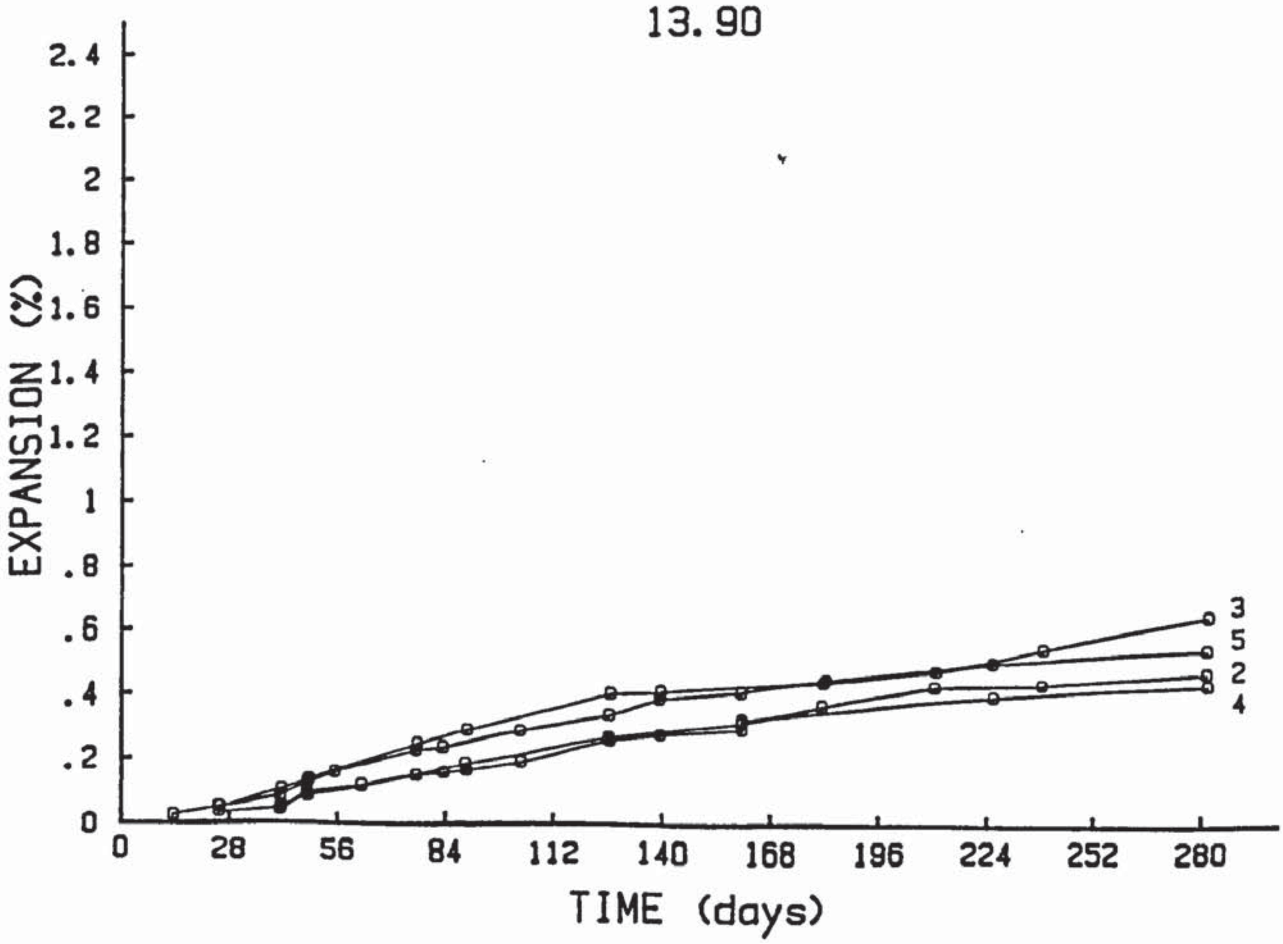
Fig 3.14

20% Pfa

Expansion (%) Vs time

40% Pfa

Fig 3.15



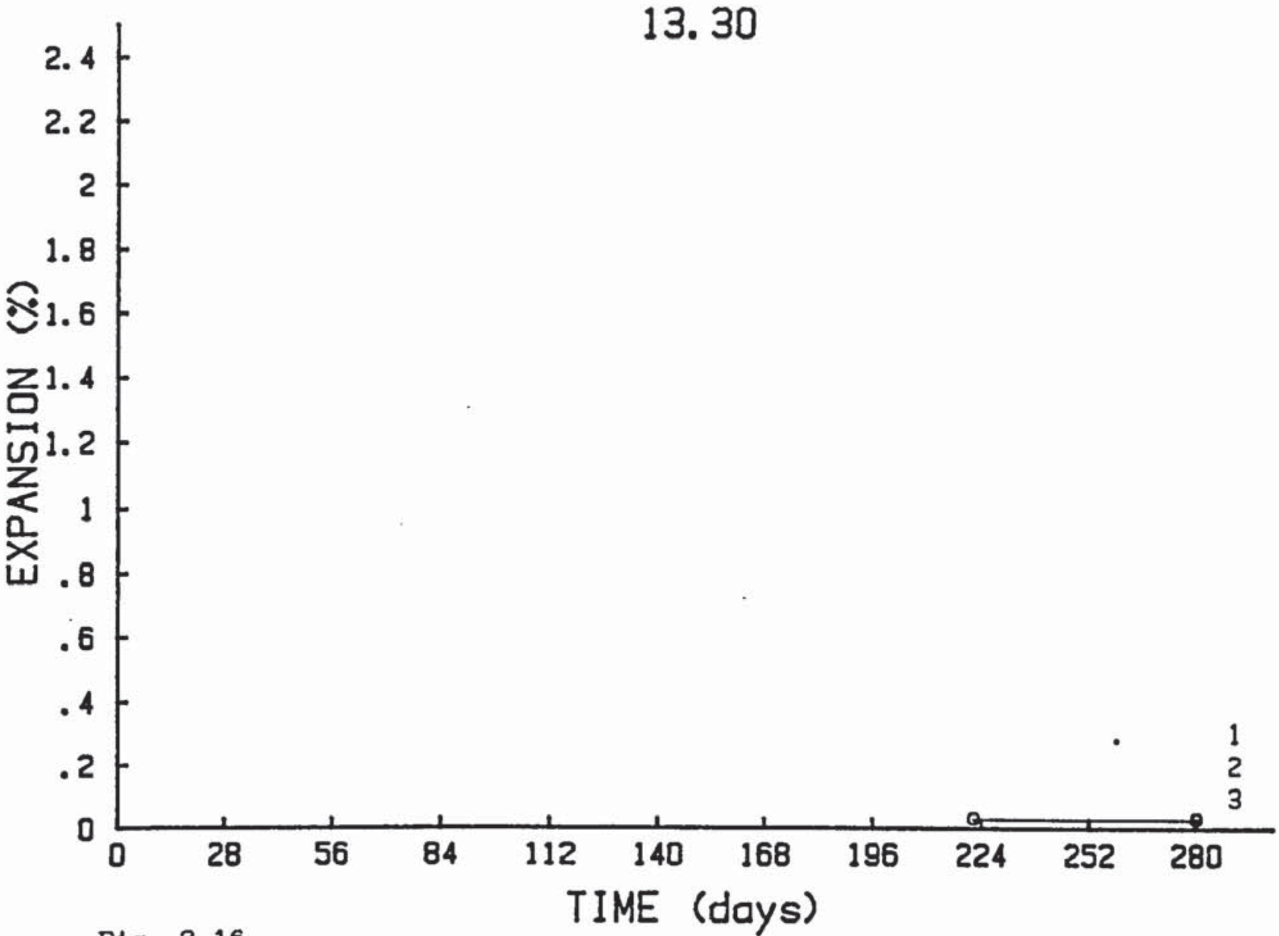


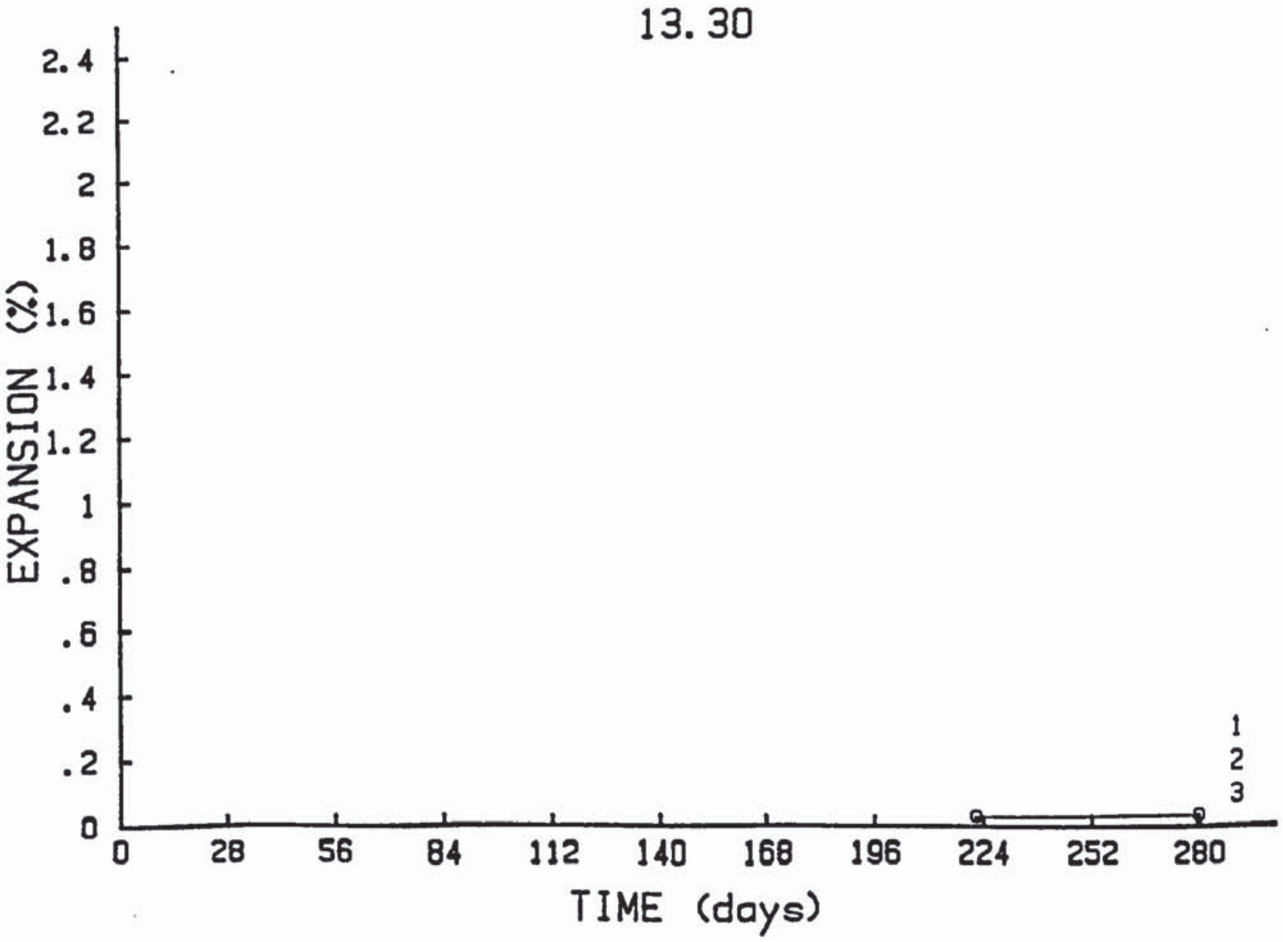
Fig 3.16

40% slag

Expansion (%) vs time slag blended cements stored under NaOH at 20°C

60% slag

Fig 3.17



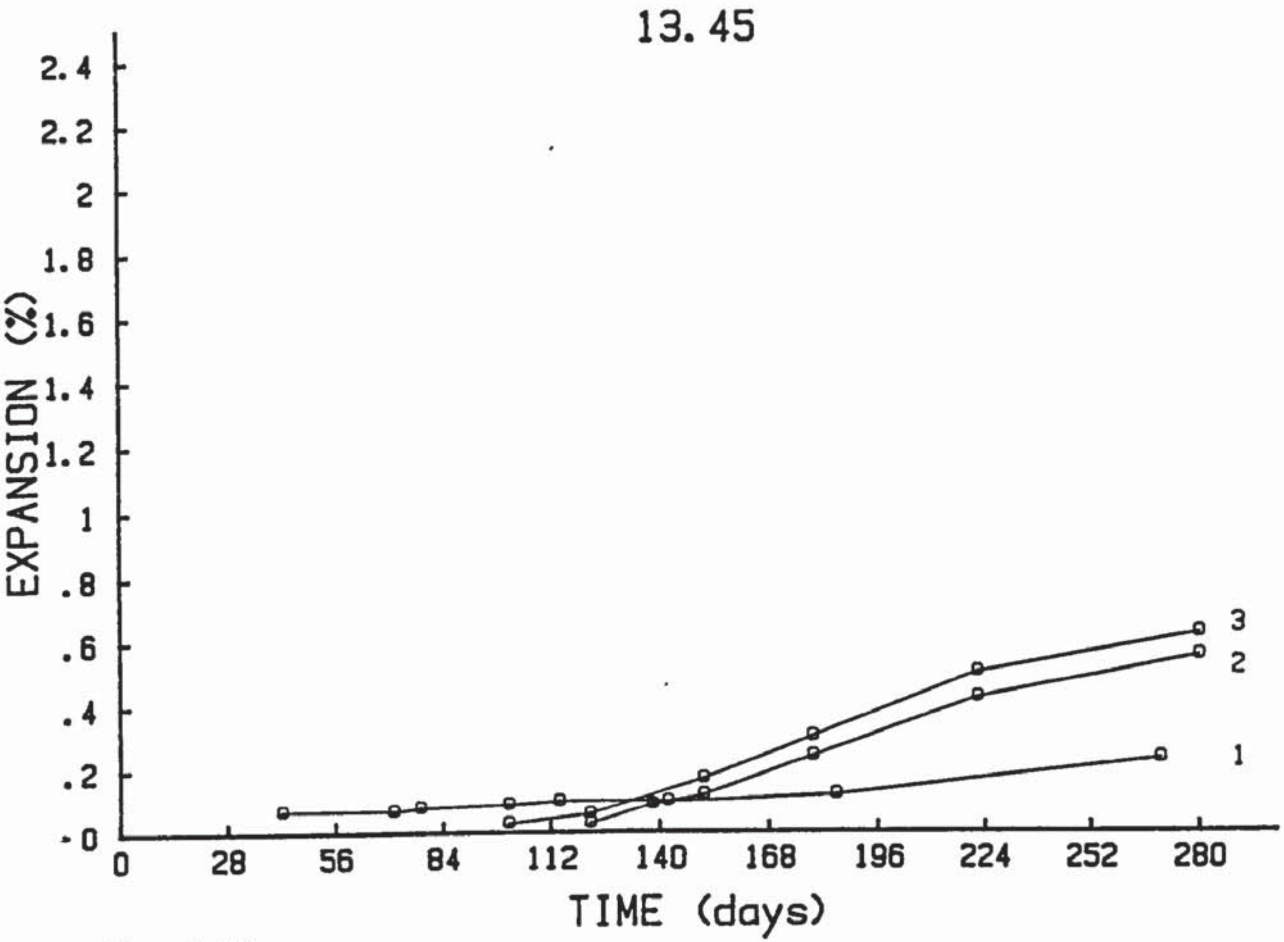


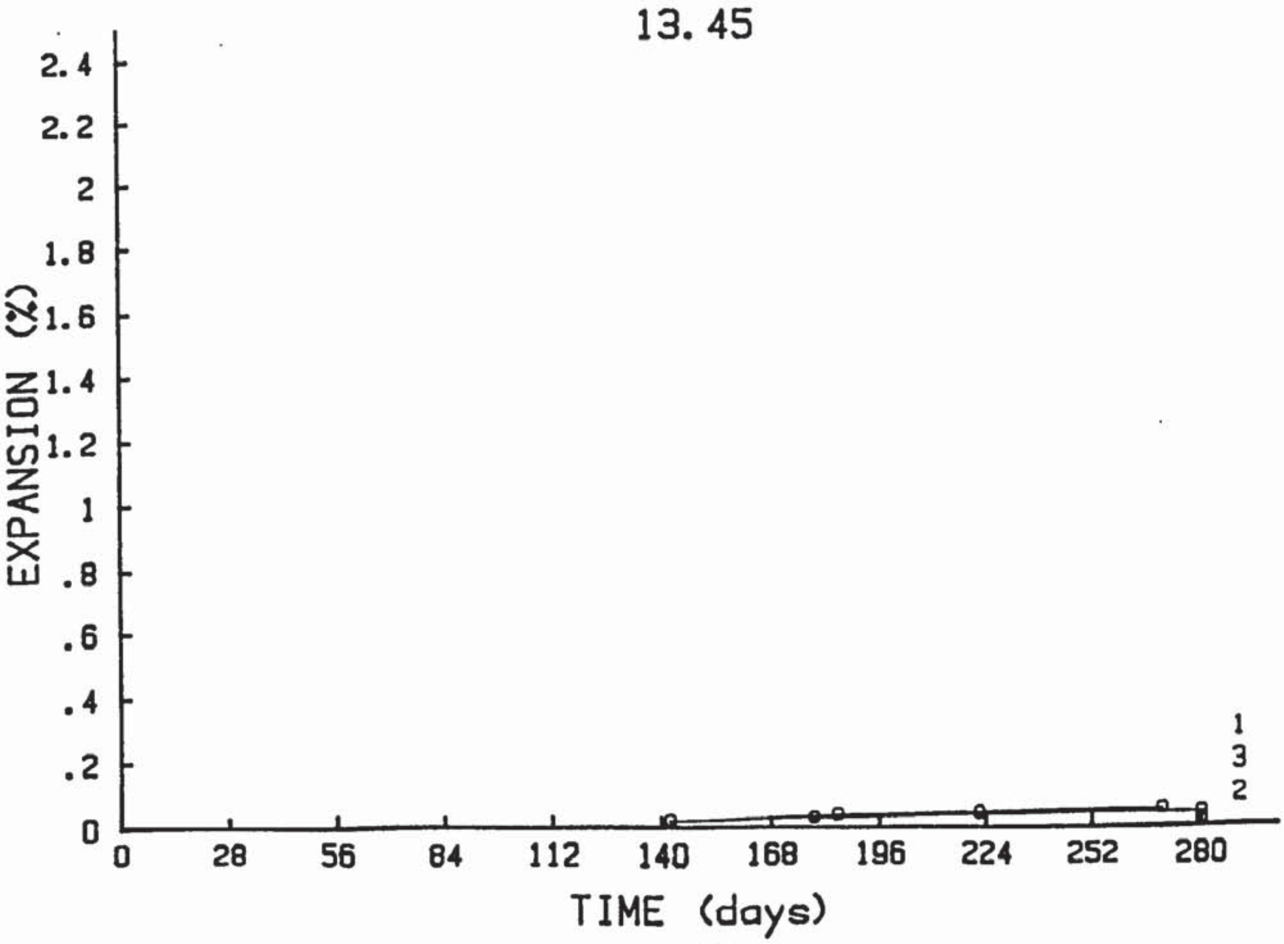
Fig 3.18

40% slag

Expansion (%) Vs time

60% slag

Fig 3.19



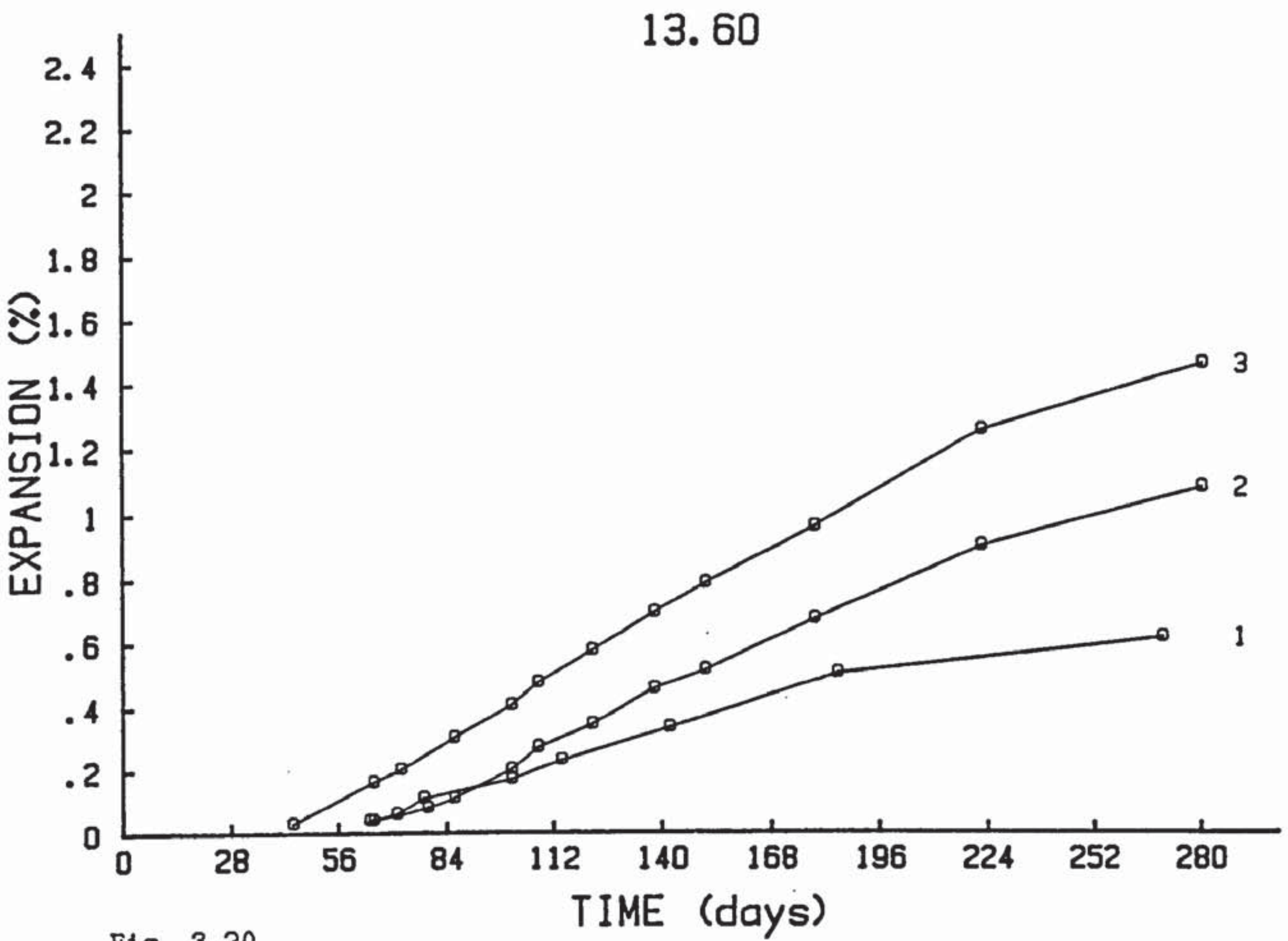


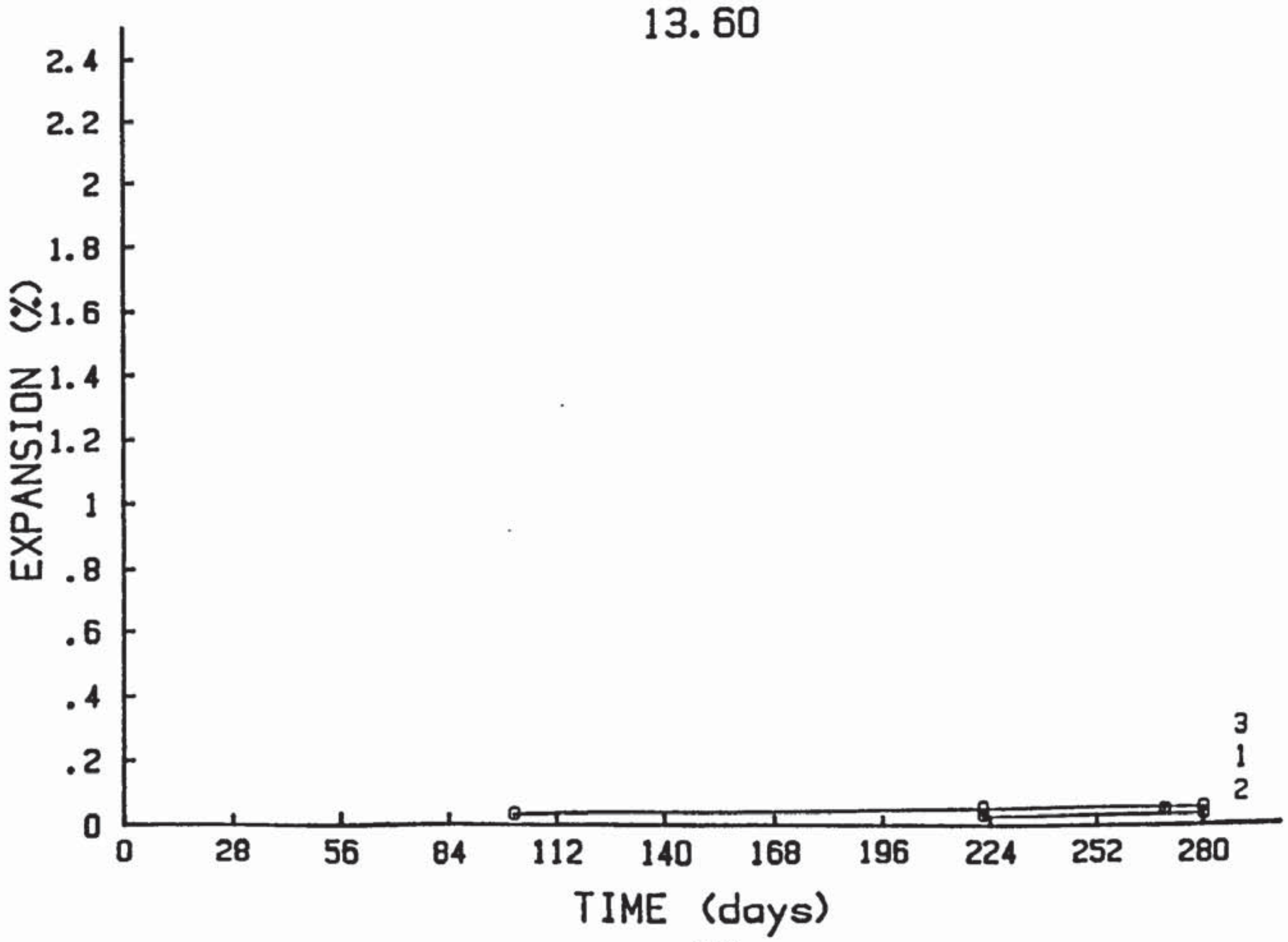
Fig 3.20

40% slag

Expansion (%) Vs time

60% slag

Fig 3.21



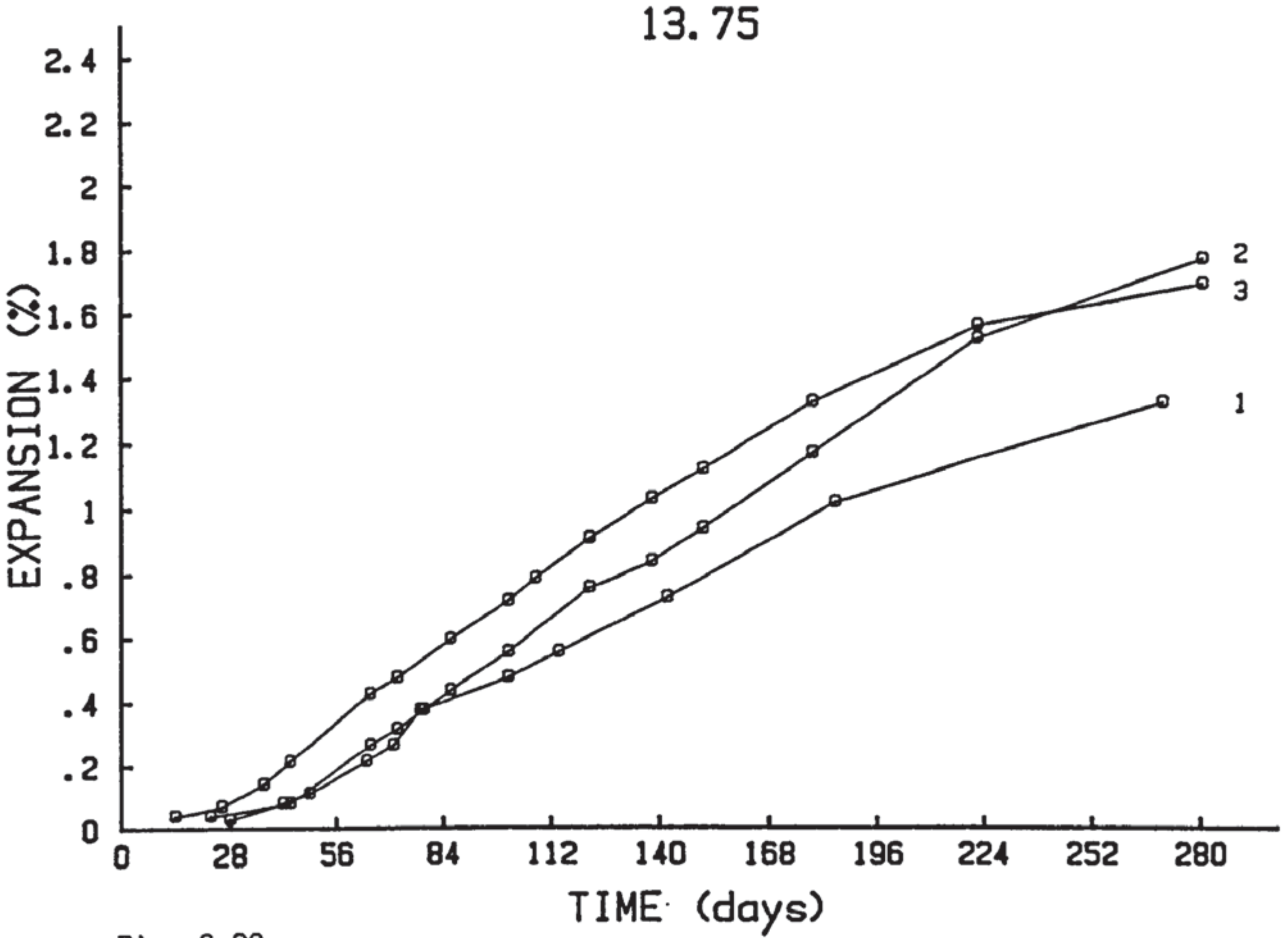


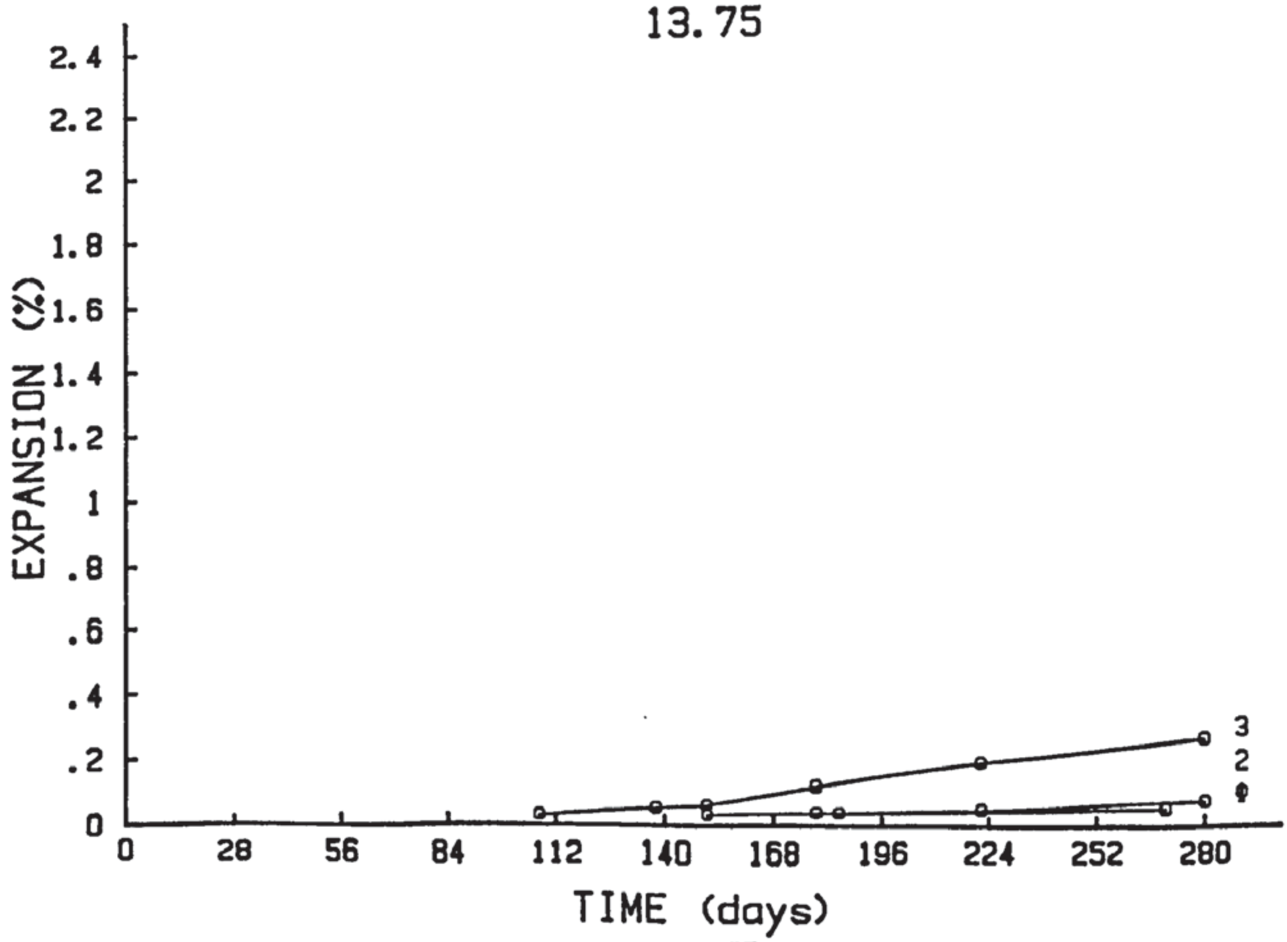
Fig 3.22

40% slag

Expansion (%) Vs time

60% slag

Fig 3.23



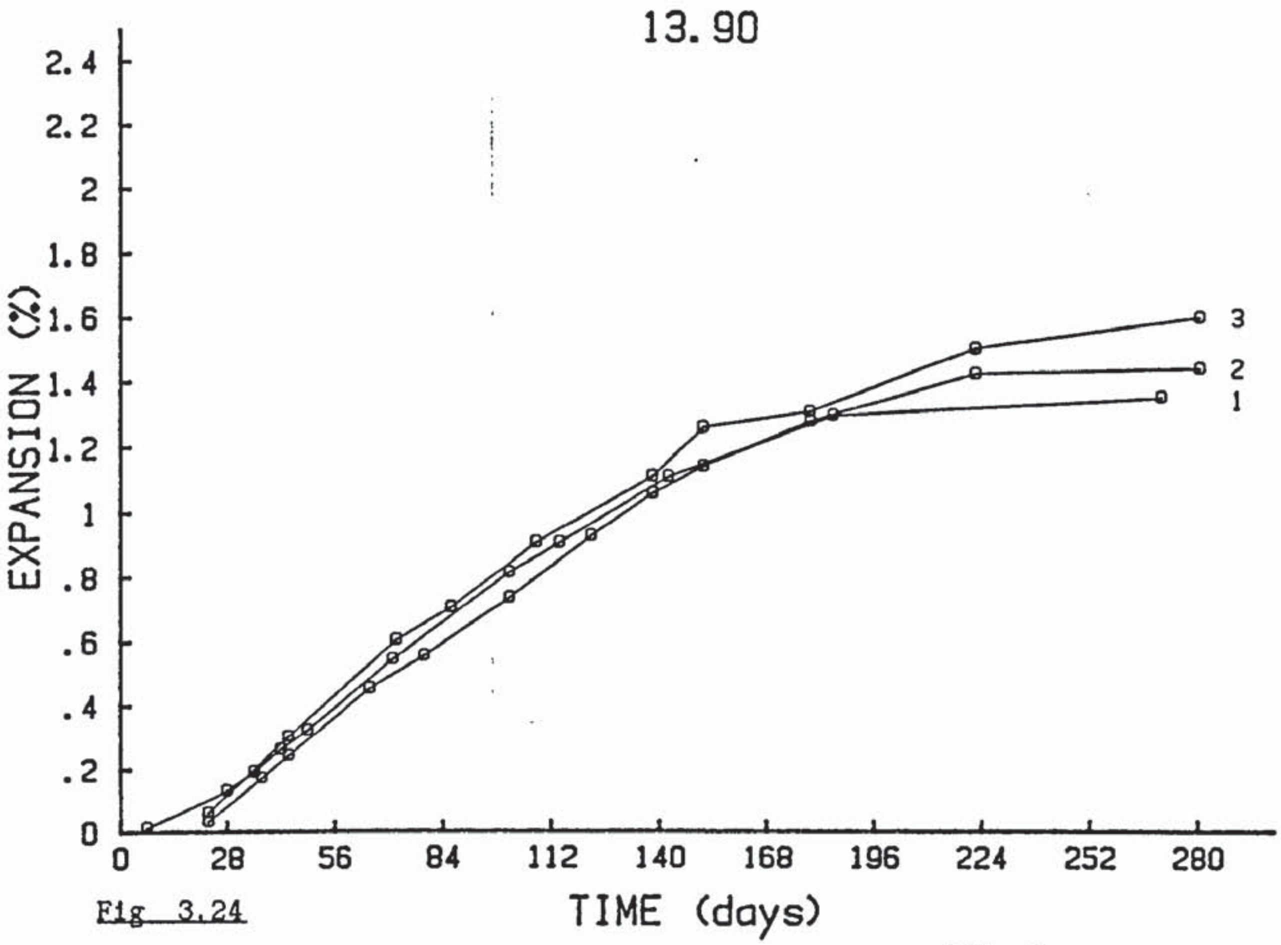


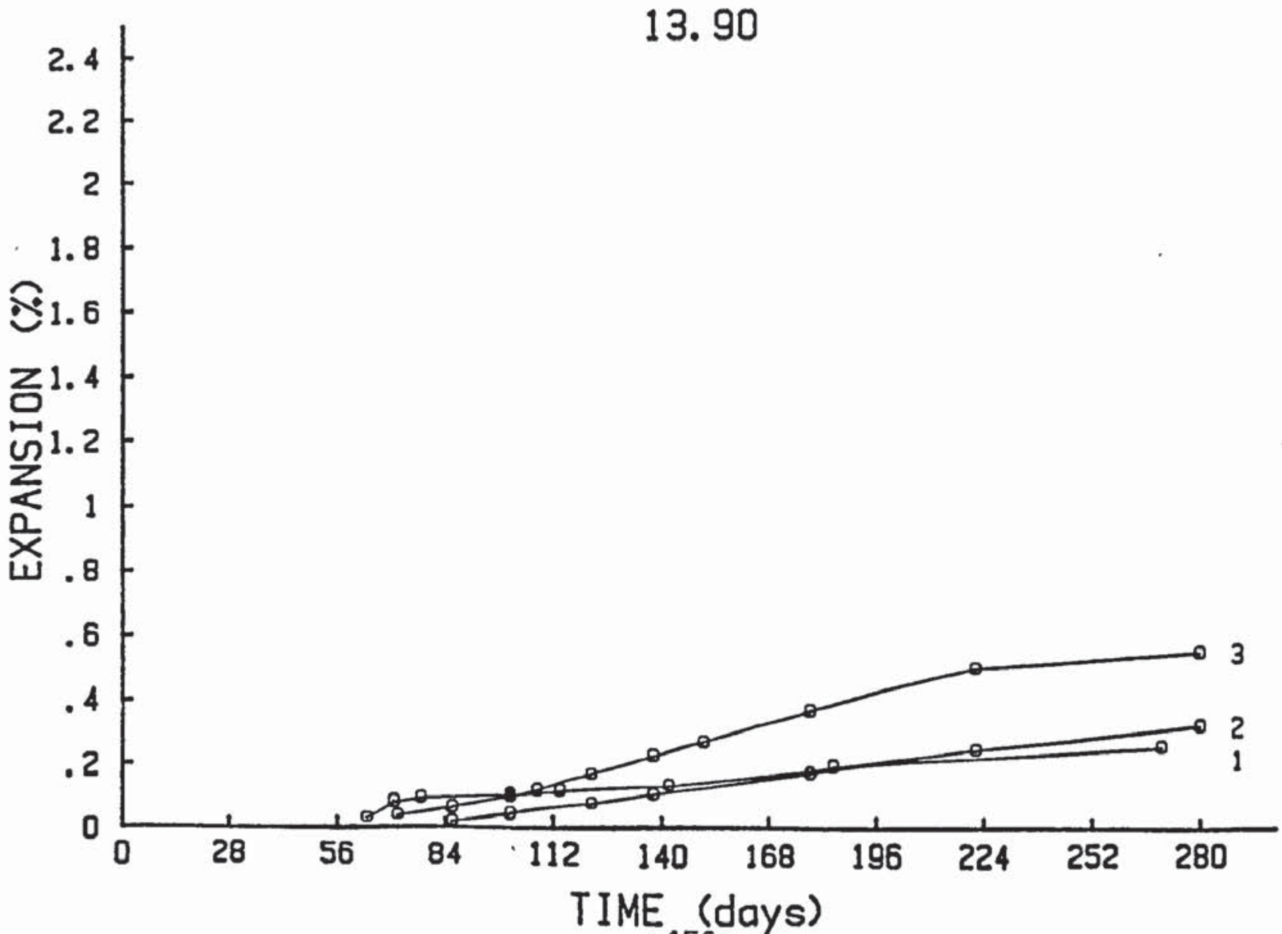
Fig 3.24

40% slag

Expansion (%) Vs time

60% slag

Fig 3.25



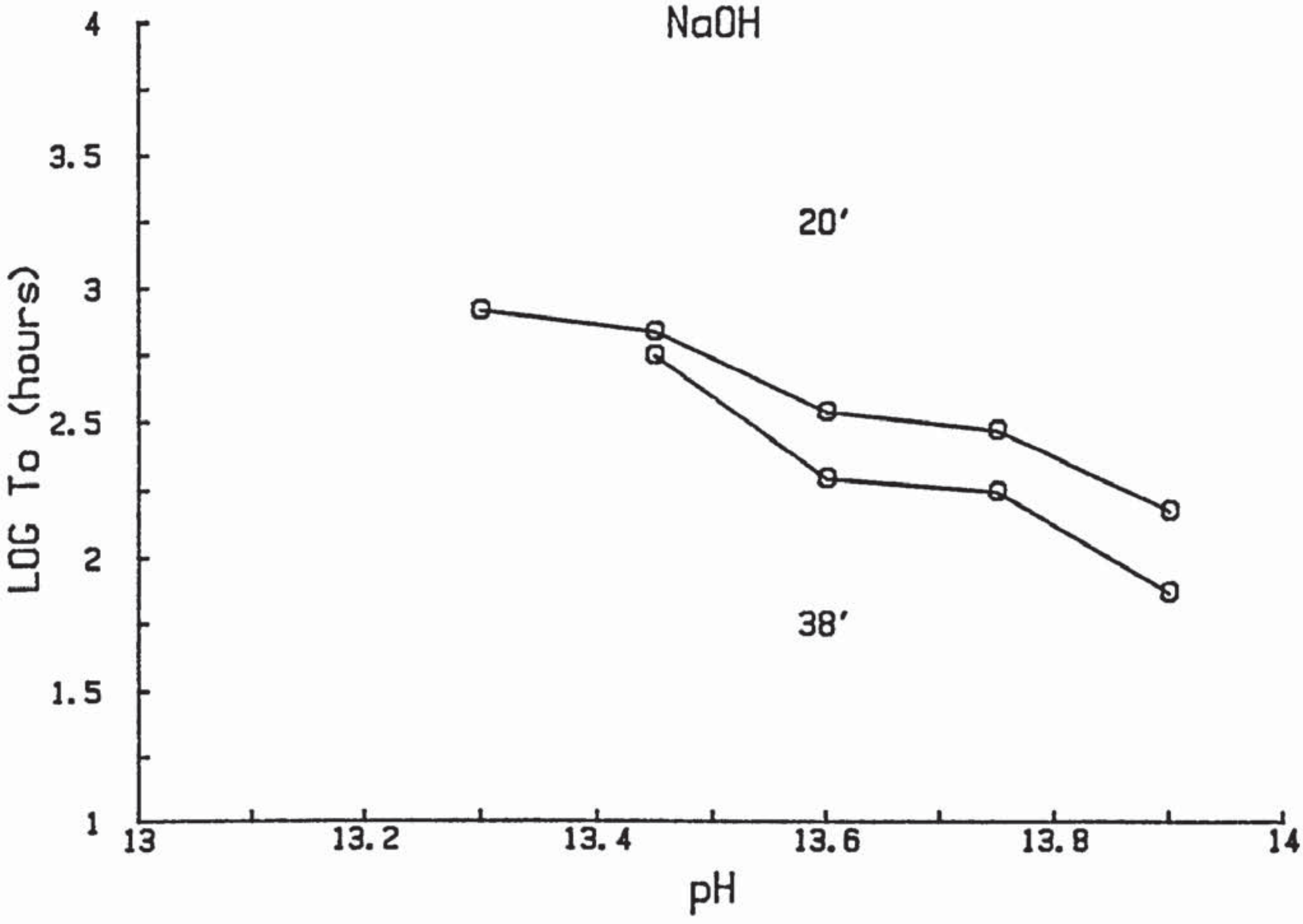
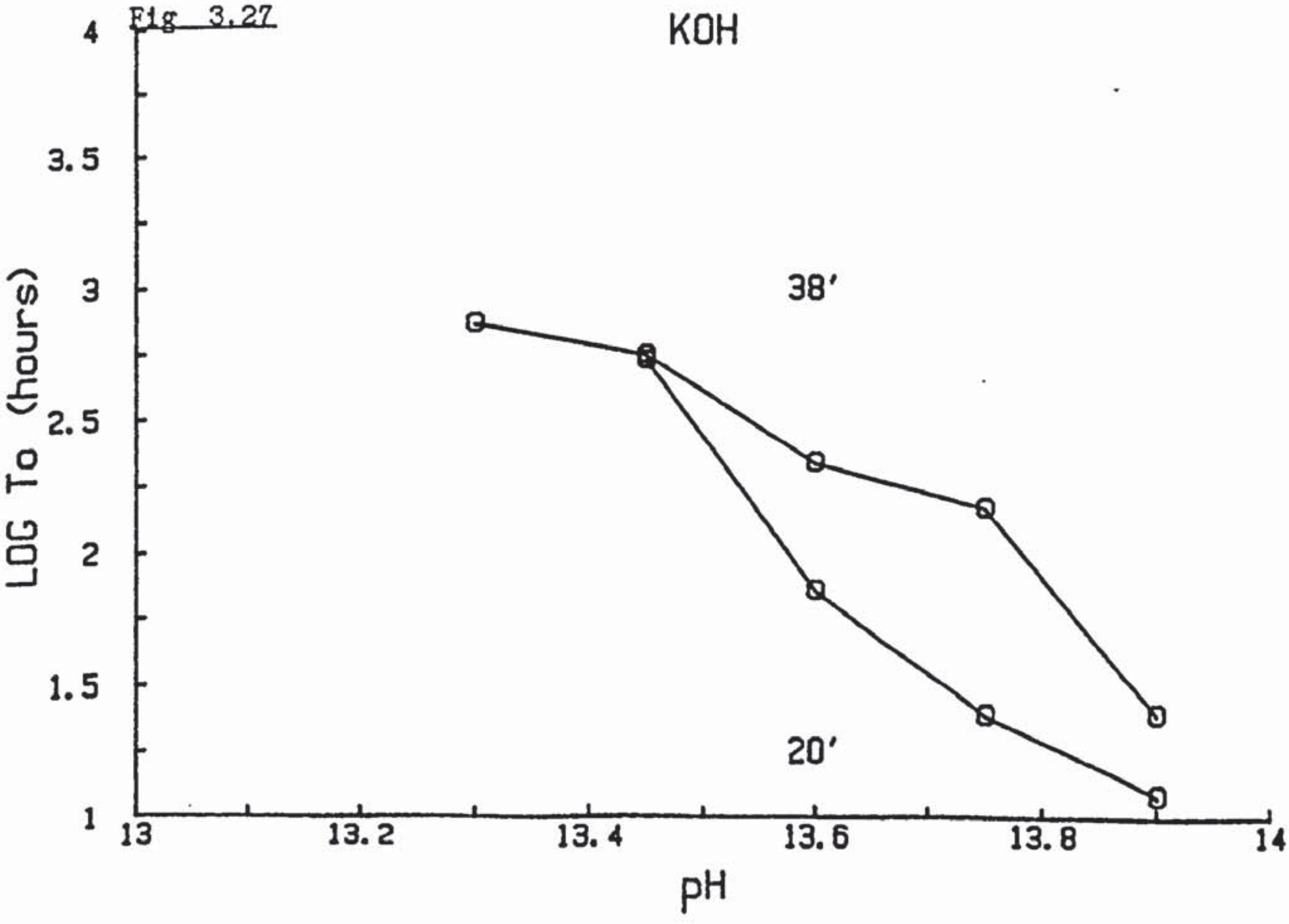


Fig 3.26

To Vs Curing solution concentration for plain cement specimens

Fig 3.27



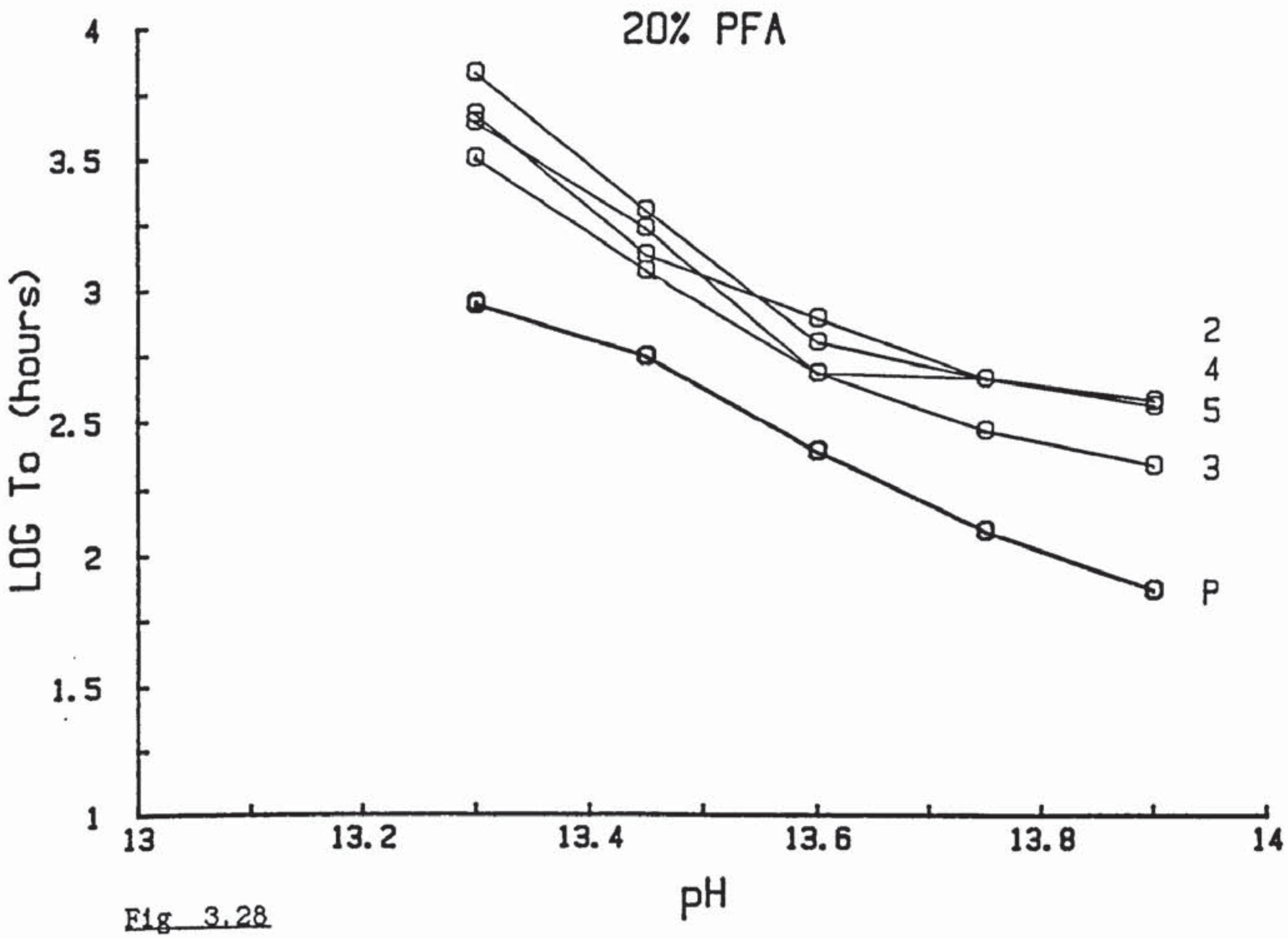
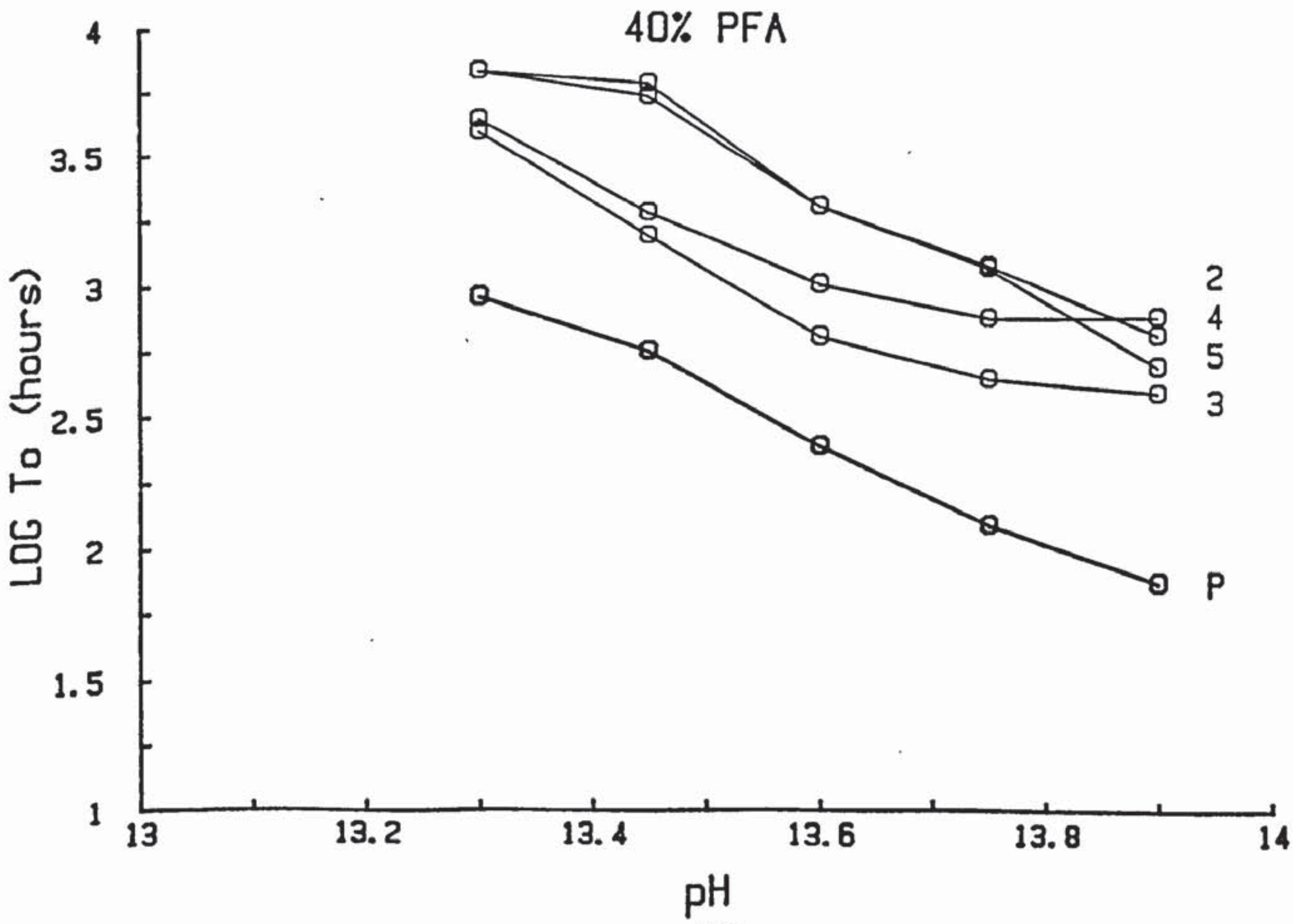


Fig 3.28

To Vs Curing solution concentration for ash blended specimens

Fig 3.29



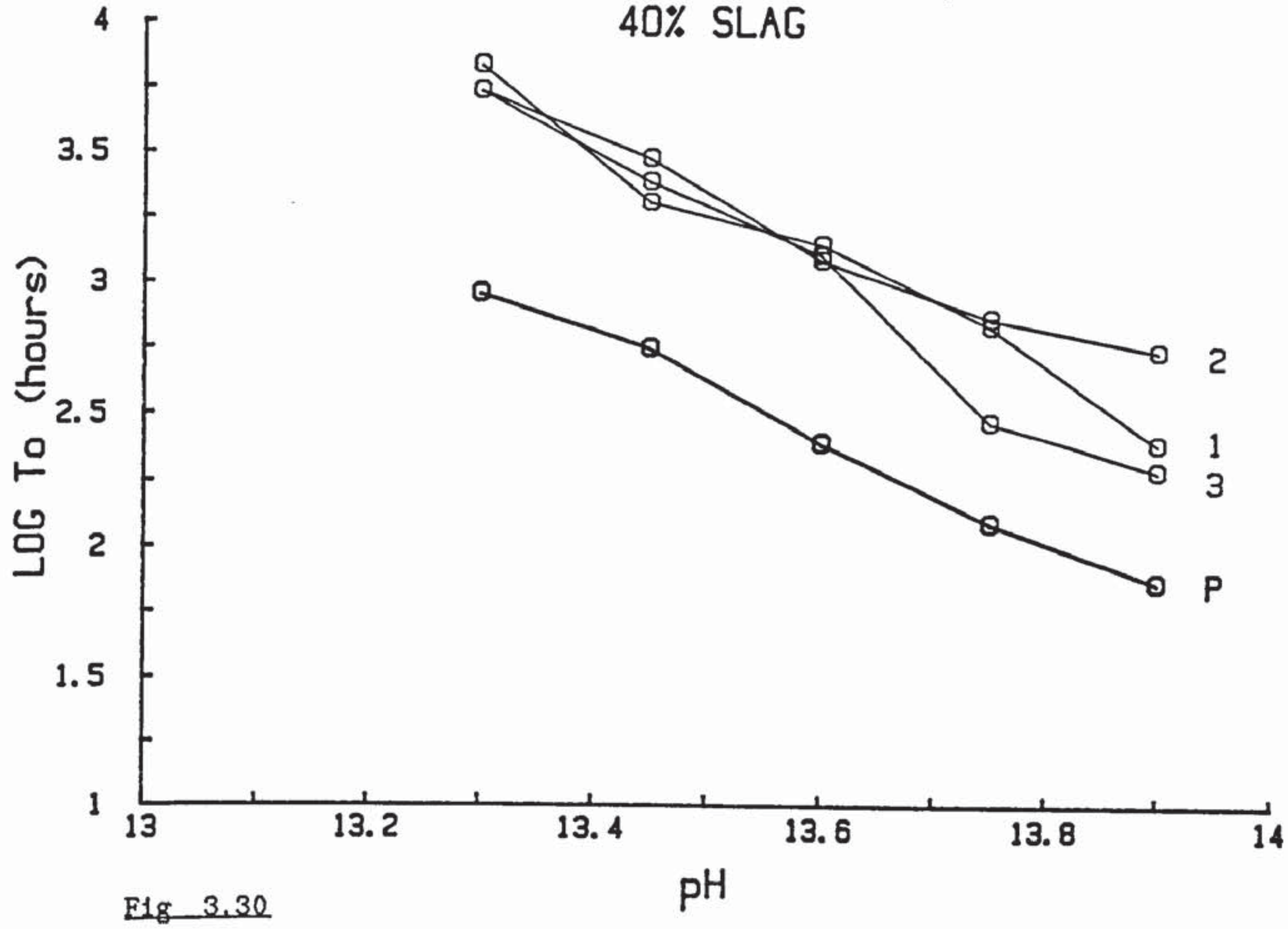
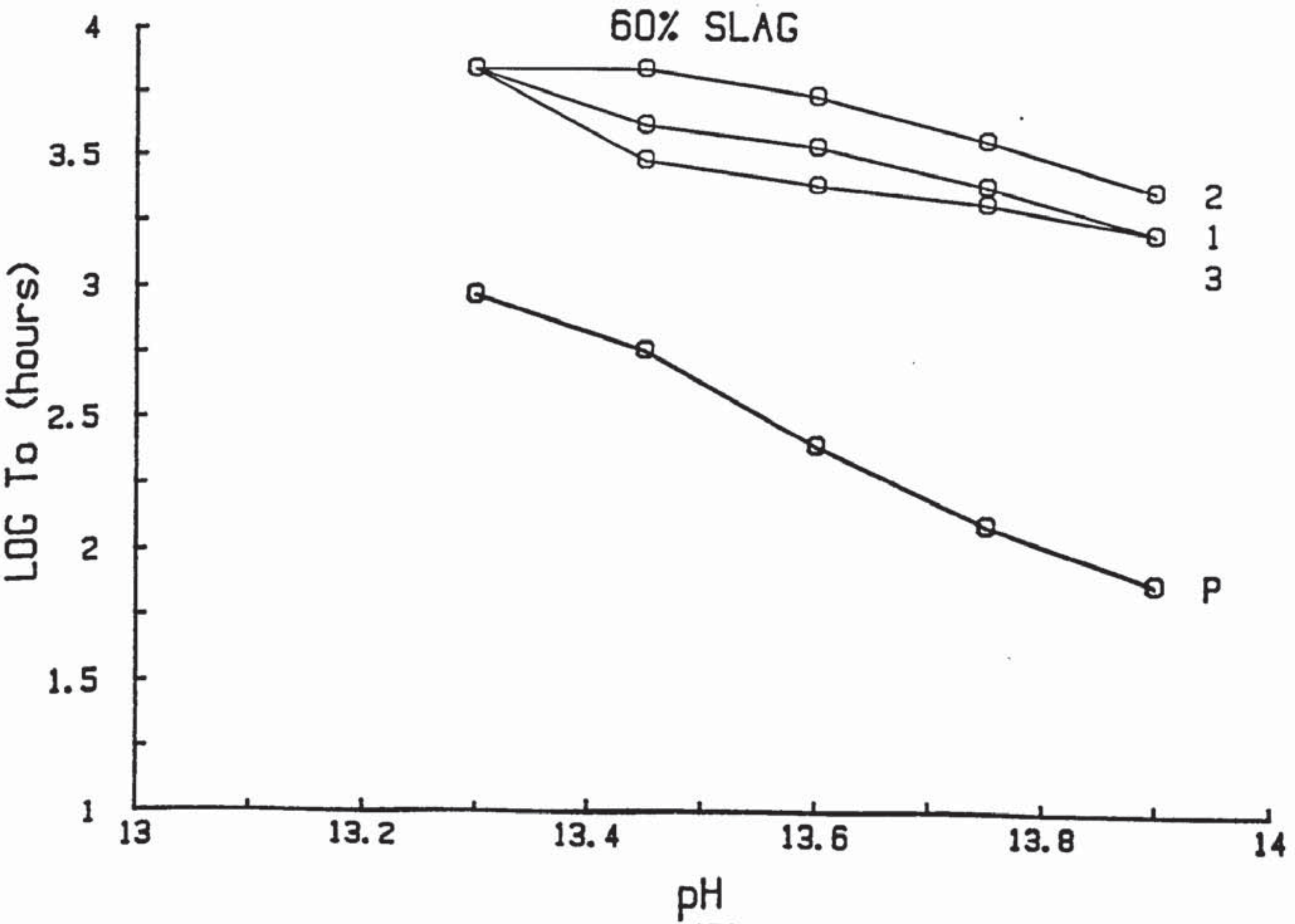


Fig 3.30

To Vs Curing solution concentration for slag blended specimens

Fig 3.31



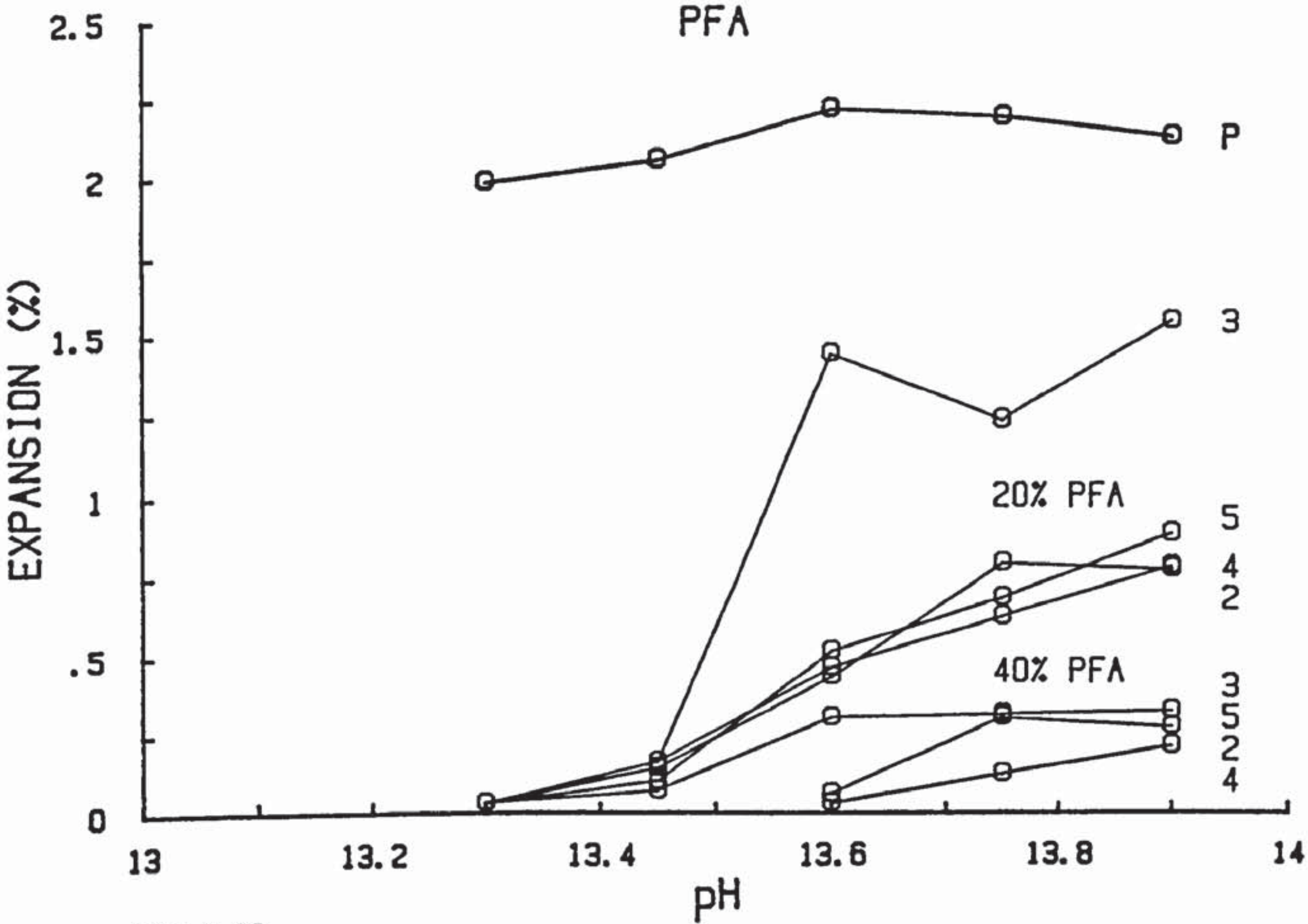
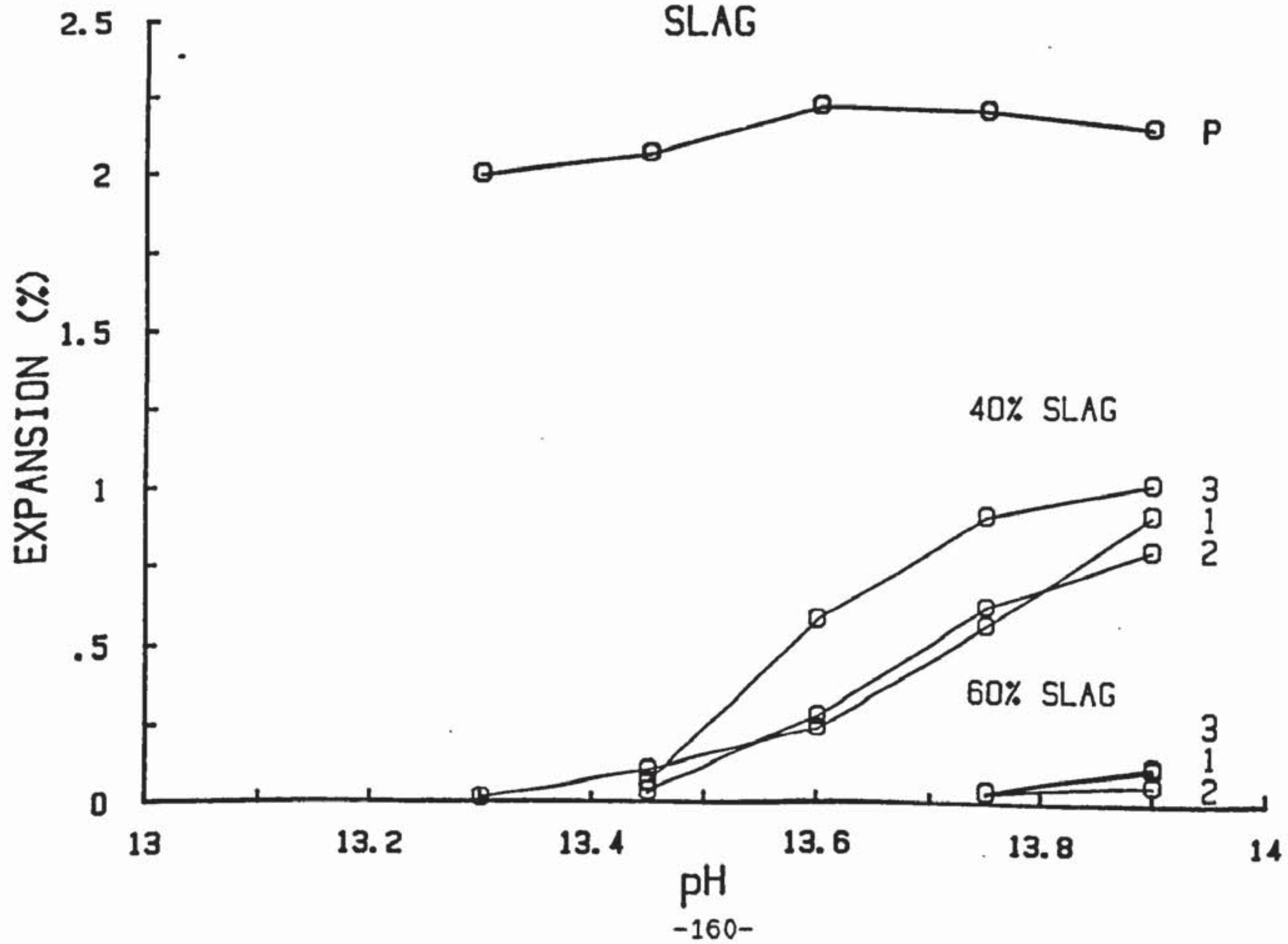


Fig 3.32

Comparison of expansion control achieved after 2688 hours by each cement blend

Fig 3.33



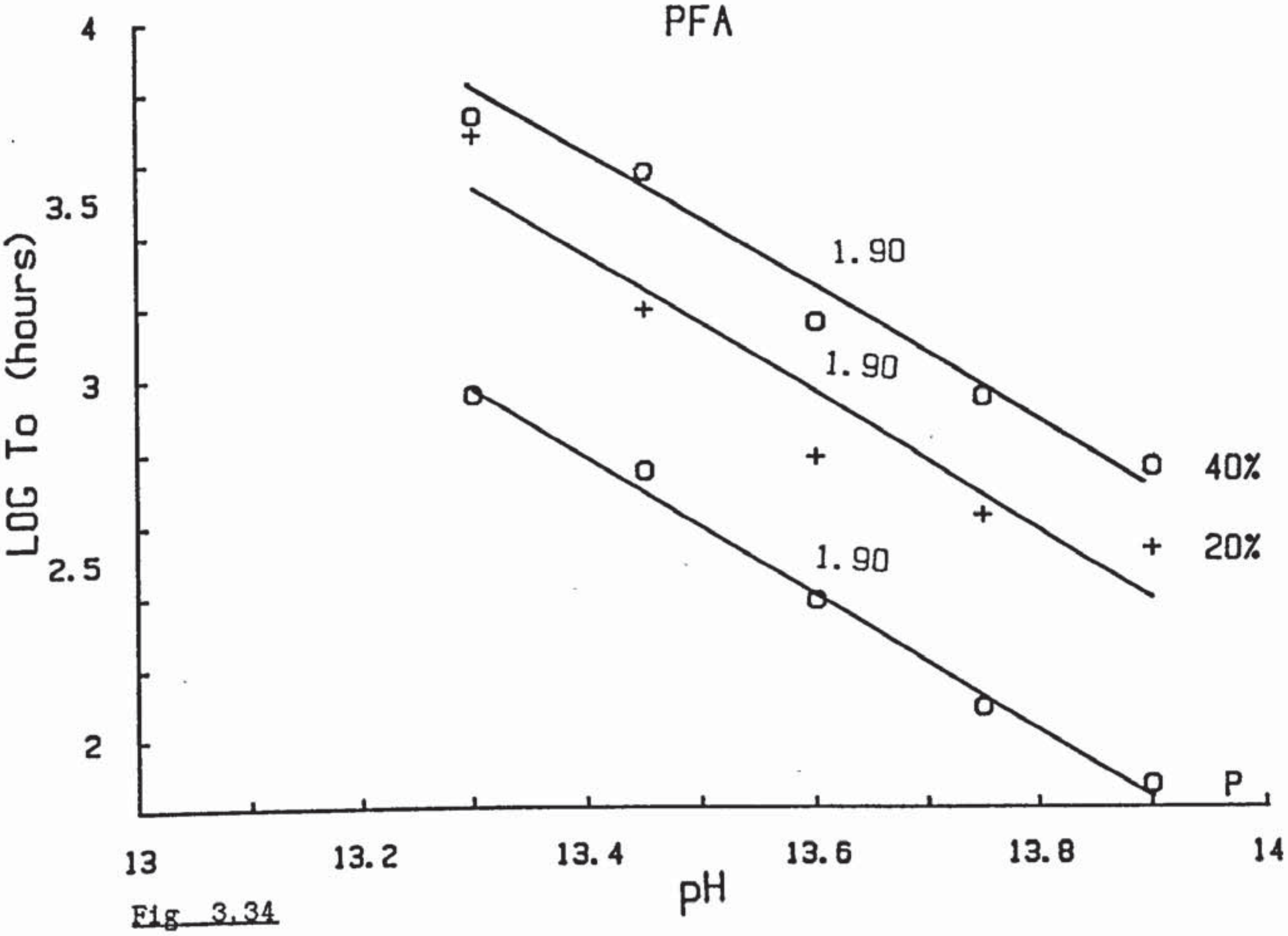
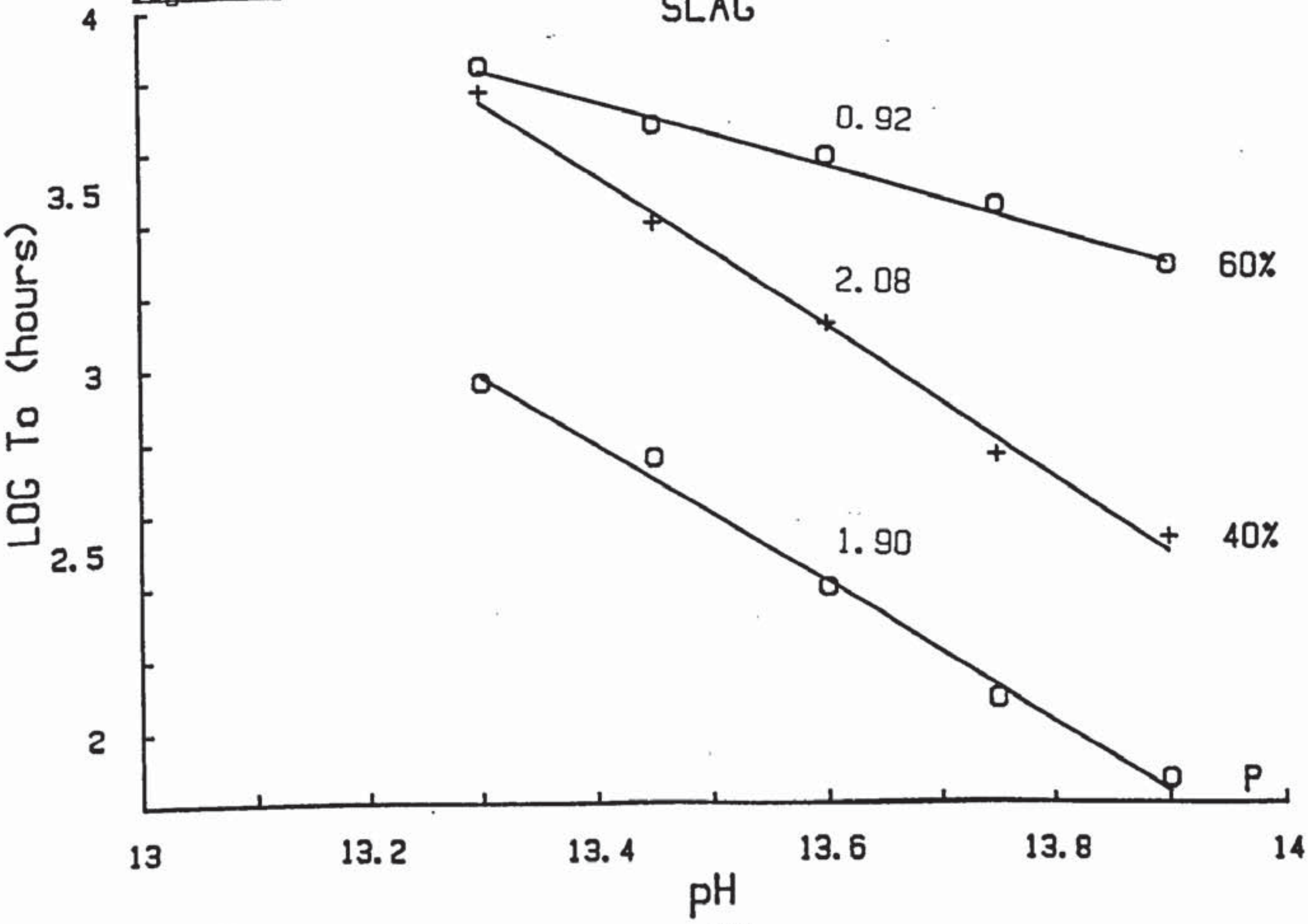


Fig 3.34

Mean To value obtained for each cement blend as a function of solution pH (with gradient of each "best fit" straight line.)

Fig 3.35



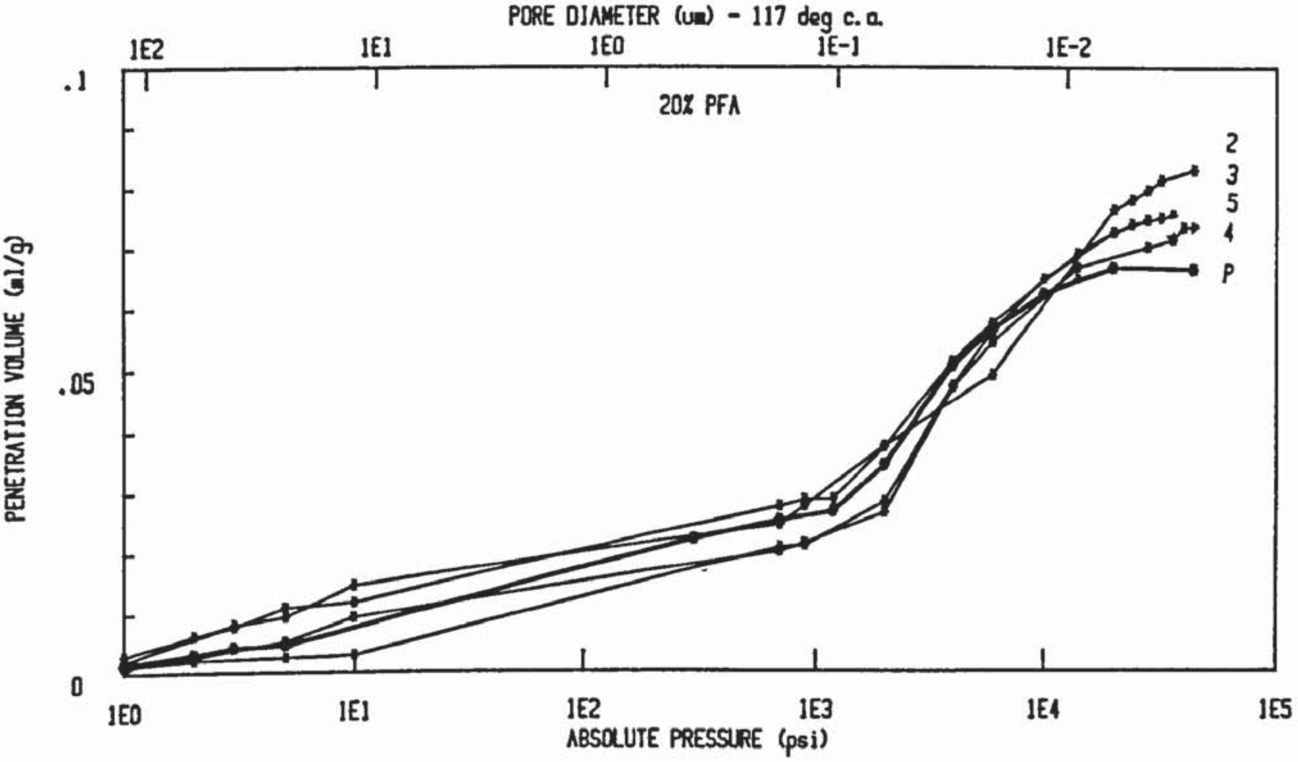
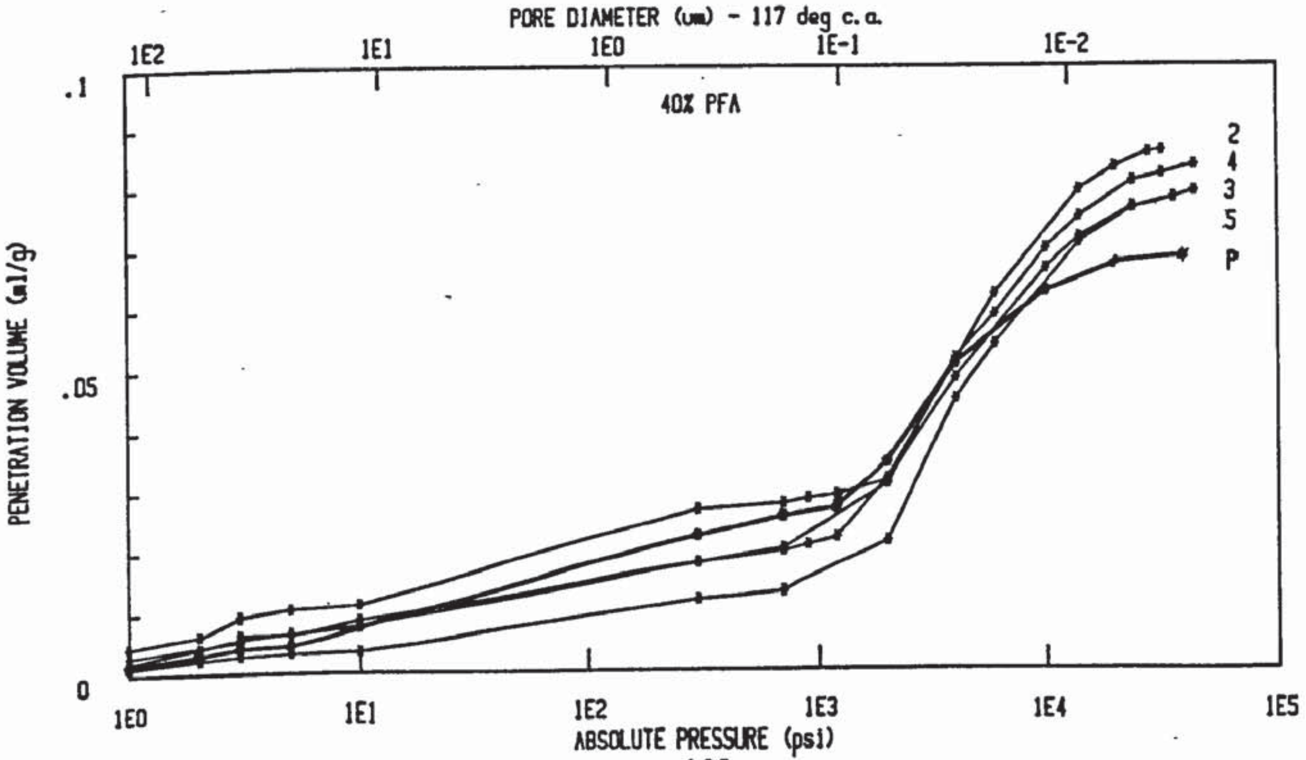


Fig 3.36

Pore size distribution of each pfa blended cement mortar

Fig 3.37



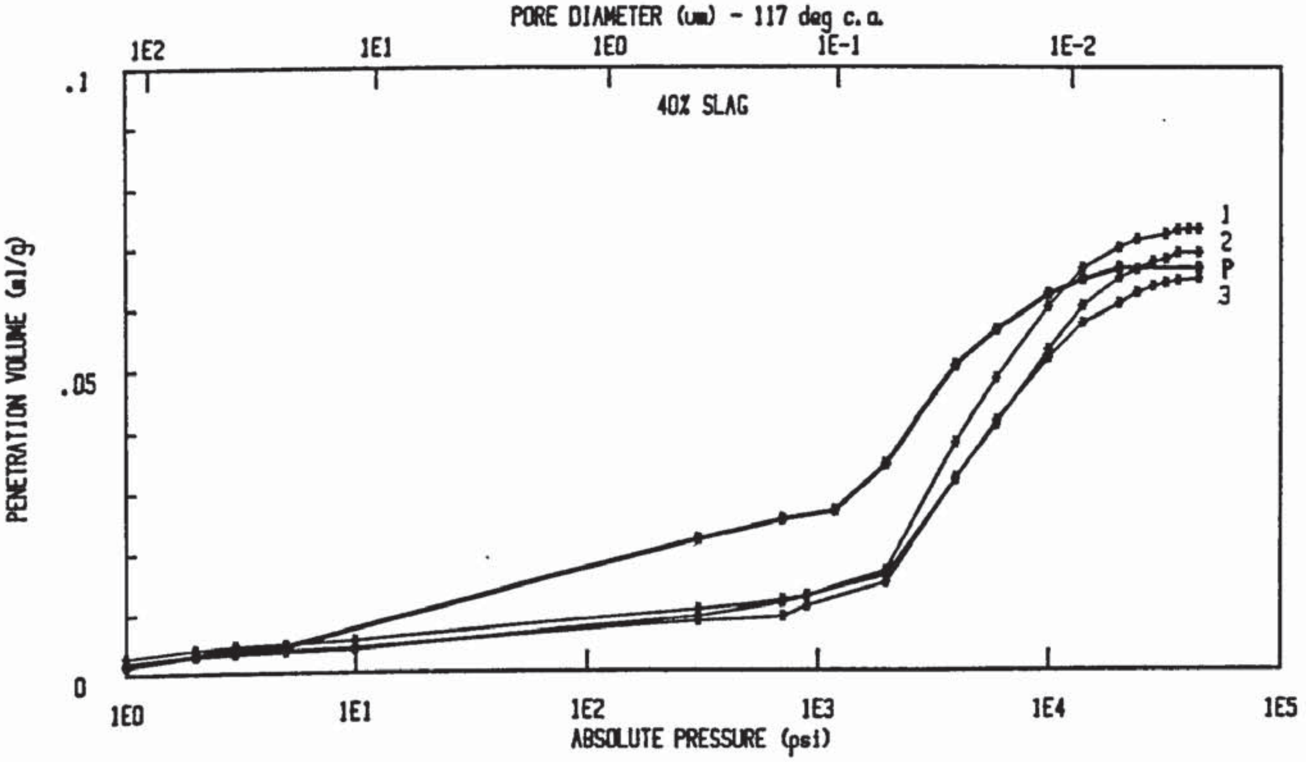
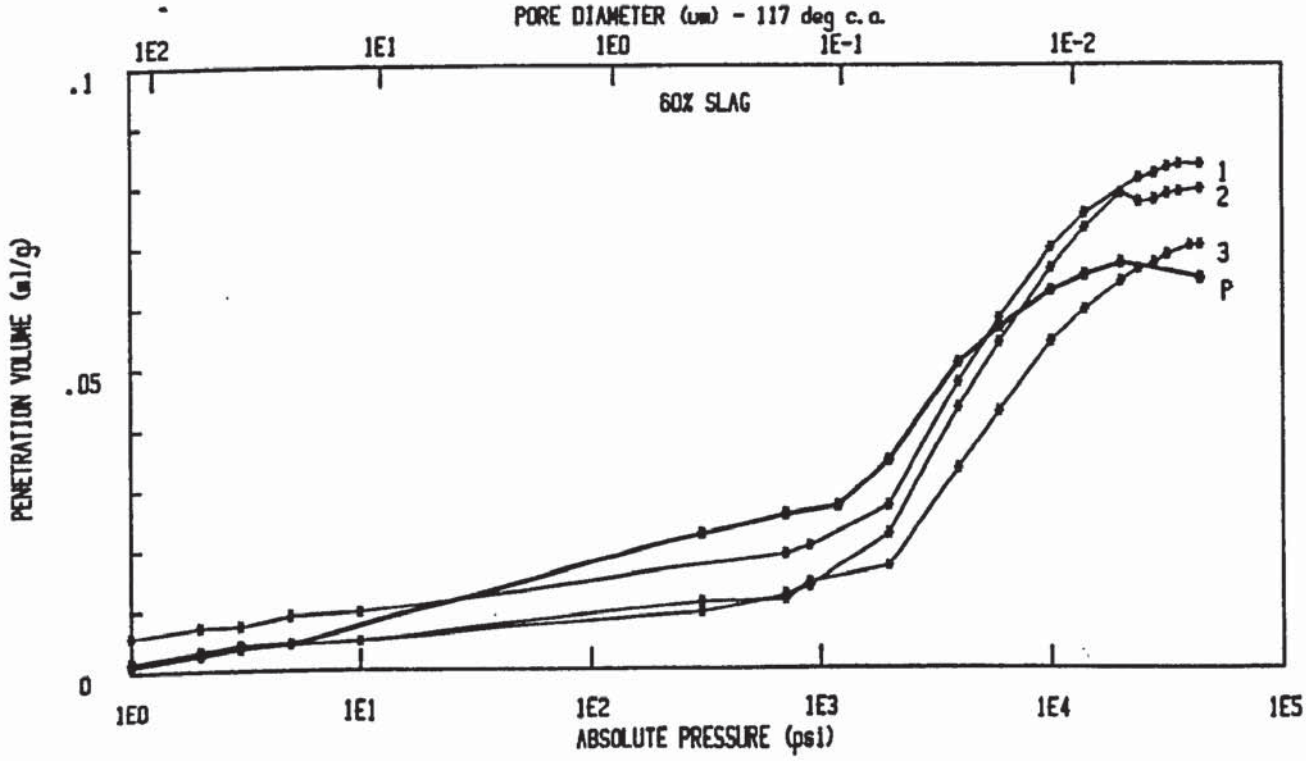


Fig 3.38

Pore size distribution of each blended cement mortar

Fig 3.39



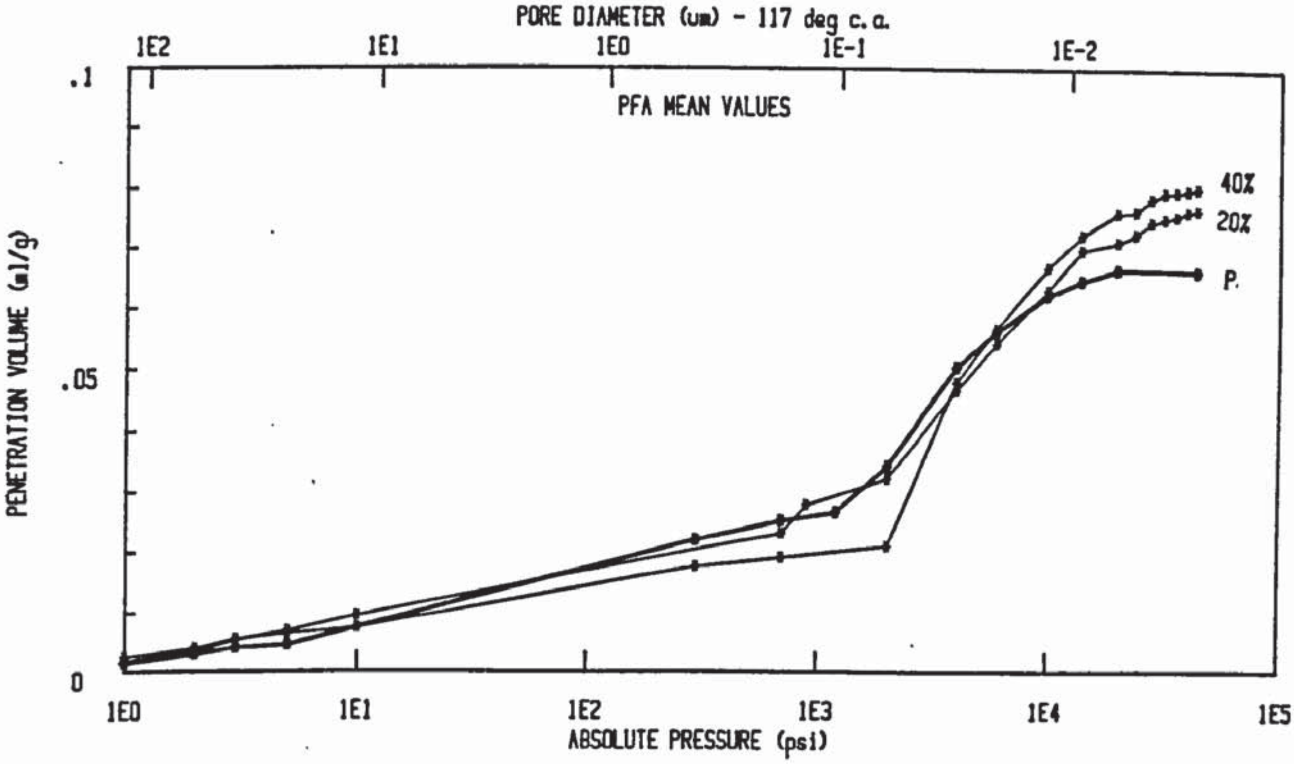


Fig 3.40

Mean value pore size distribution of plain and blended cements

Fig 3.41

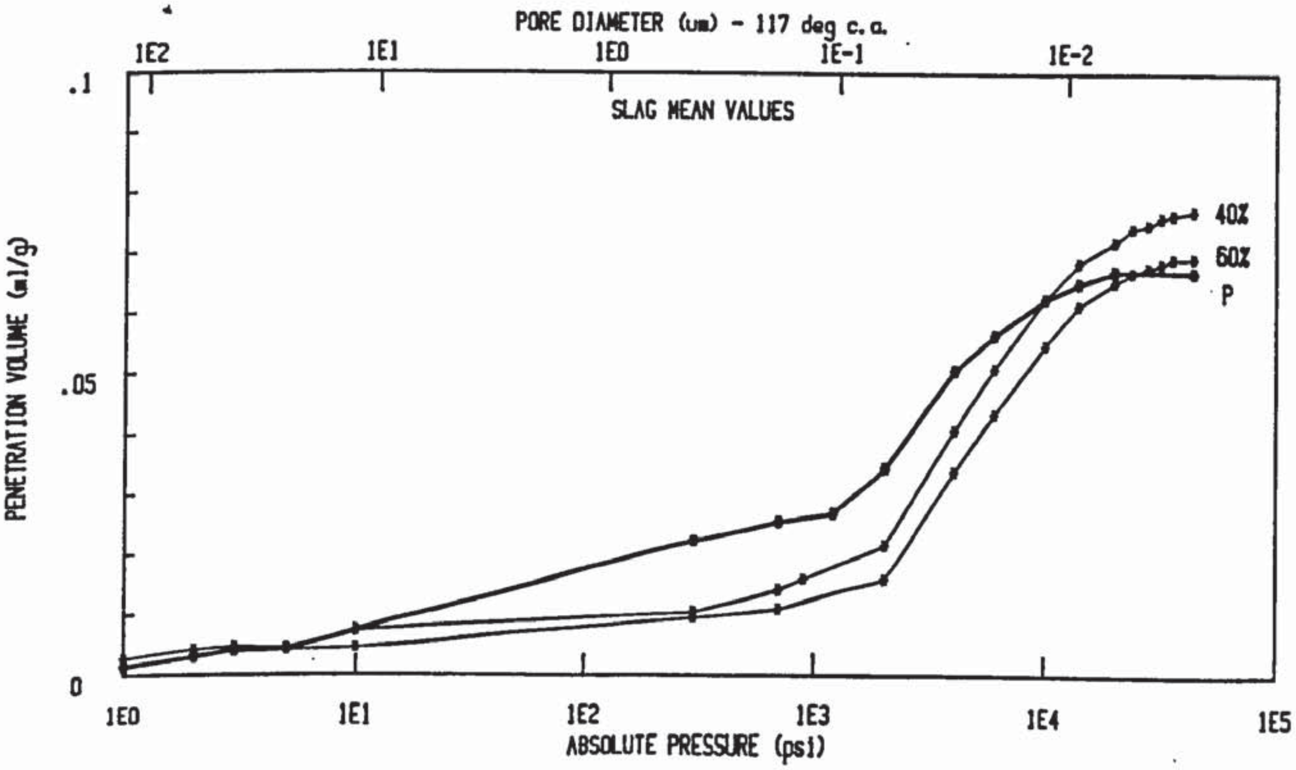


Table 3.24 OH diffusion coefficient for plain cement

Time (seconds)	Hydroxyl ion concentration mols/l				
	Disc A	Disc B	Disc C	Disc D	Disc E
86 400	0.041	0.038	0.038	0.040	0.040
259 200	0.049	0.040	0.042	0.044	0.041
432 000	0.052	0.052	0.044	0.052	0.046
604 800	0.058	0.054	0.050	0.062	0.052
777 600	0.065	0.061	0.052	0.066	0.060
1 036 800	0.075	0.064	0.058	0.071	0.062

Volume of Cell (cm^3)	85	80	84	75	80
Thickness of disc (cm)	0.31	0.31	0.35	0.32	0.34
Surface Area (cm^2)	8.042	8.042	8.042	8.042	0.042
Gradient (x E8)	3.58	2.10	2.10	3.16	2.10
Correlation	0.991	0.939	0.988	0.965	0.948
D Value (x E8)	11.20	6.48	7.68	9.43	7.10

Mean D Value	8.70 E -8
Standard Dev.	1.79 E -8

Table 3.25 OH Diffusion coefficient for pfa 2

Time (seconds)	Hydroxyl ion concentration			mols/l
	Disc A	Disc B	Disc C	Disc D
950 400	0.050	0.044	0.046	0.048
1 814 400	0.053	0.048	0.048	0.051
2 678 400	0.057	0.054	0.054	0.052
3 801 600	0.066	0.060	0.065	0.063
4 579 200	0.073	0.075	0.070	0.077

Volume of Cell (cm^3)	80	85	85	80
Thickness of disc (cm)	0.32	0.33	0.33	0.32
Surface Area (cm^2)	8.042	8.042	8.042	8.042
Gradient (x E9)	7.23	6.79	6.89	7.72
Correlation	0.985	0.997	0.969	0.863
D Value (x E8)	2.30	2.37	2.40	2.46

Mean D Value	2.38 E -8
Standard Dev.	0.06 E -8

Table 3.26 OH Diffusion coefficient for pfa 3

Time (seconds)	Hydroxyl ion concentration			mols/l
	Disc A	Disc B	Disc C	Disc D
950 400	0.046	0.042	0.044	0.048
1 814 400	0.052	0.048	0.048	0.050
2 678 400	0.054	0.050	0.050	0.052
3 801 600	0.056	0.052	0.052	0.055
4 579 200	0.058	0.053	0.055	0.056

Volume of Cell (cm^3)	86	80	85	80
Thickness of disc (cm)	0.34	0.33	0.33	0.33
Surface Area (cm^2)	8.042	8.042	8.042	8.042
Gradient (x E9)	1.81	1.81	2.53	2.76
Correlation	0.988	0.988	0.975	0.971
D Value (x E9)	6.58	5.94	8.82	9.06

Mean D Value	7.60 E -9
Standard Dev.	1.36 E -9

Table 3.27 OH Diffusion Coefficient for pfa 4

Time (seconds)	Hydroxyl ion concentration mols/l				
	Disc A	Disc B	Disc C	Disc D	Disc E
1 296 000	0.036	0.041	0.039	0.038	0.042
1 900 800	0.042	0.043	0.043	0.041	0.043
2 505 600	0.044	0.046	0.046	0.046	0.047
3 110 400	0.047	0.050	0.047	0.047	0.048
5 011 200	0.054	0.054	0.054	0.054	0.057

Volume of Cell (cm^3)	80	100	80	80	80
Thickness of disc (cm)	0.32	0.32	0.32	0.33	0.32
Surface Area (cm^2)	8.042	8.042	8.042	8.042	8.042
Gradient (x E9)	3.86	3.50	3.77	4.31	4.31
Correlation	0.997	0.949	0.974	0.964	0.983
D Value (x E8)	1.23	1.39	1.20	1.41	1.37

Mean D Value	1.32 E -8
Standard Dev.	0.09 E -8

Table 3.28 OH Diffusion coefficient for pfa 5

Time (seconds)	Hydroxyl ion concentration mols/l				
	Disc A	Disc B	Disc C	Disc D	Disc E
1 296 000	0.042	0.045	0.046	0.043	0.047
1 900 800	0.046	0.048	0.047	0.047	0.049
2 505 600	0.055	0.053	0.053	0.057	0.053
3 110 400	0.056	0.056	0.056	0.057	0.056
5 011 200	0.071	0.070	0.069	0.069	0.067

Volume of Cell (cm^3)	80	80	80	80	80
Thickness of disc (cm)	0.33	0.33	0.32	0.33	0.33
Surface Area (cm^2)	8.042	8.042	8.042	8.042	8.042
Gradient (x E9)	7.54	7.07	6.75	7.07	6.75
Correlation	0.977	0.996	0.986	0.996	0.996
D Value (x E8)	2.48	2.32	2.15	2.32	2.22

Mean D Value	2.30 E -8
Standard Dev.	0.11 E -8

Table 3.29 Na diffusion coefficient for plain cement

Time (seconds)	Sodium ion concentration		mols/l		
	Disc A	Disc B	Disc C	Disc D	Disc E
86 400	0.035	0.037	0.038	0.038	0.040
259 200	0.040	0.040	0.039	0.039	0.039
432 000	0.052	0.045	0.044	0.052	0.046
604 800	0.066	0.052	0.050	0.060	0.052
777 600	0.072	0.055	0.055	0.070	0.055
1 036 800	0.077	0.061	0.058	0.075	0.061

Volume of Cell (cm^3)	85	80	84	75	80
Thickness of Disc (cm)	0.31	0.31	0.35	0.32	0.34
Surface Area (cm^2)	8.042	8.042	8.042	8.042	8.042
Gradient (x E8)	3.16	2.10	2.10	4.21	2.10
Correlation	0.977	0.987	0.963	0.950	0.974
D Value (x E8)	10.4	6.48	7.68	12.6	7.10

Mean D Value	8.85 E -8
Standard Dev.	2.30 E -8

Table 3.30 Na diffusion coefficient pfa 2

Time (seconds)	Sodium ion concentration			mols/l
	Disc A	Disc B	Disc C	Disc D
950 400	0.064	0.055	0.060	0.061
1 814 400	0.074	0.065	0.067	0.060
2 678 400	0.080	0.069	0.071	0.071
3 801 600	0.085	0.076	0.078	0.080
4 579 200	0.093	0.086	0.083	0.089

Volume of Cell (cm^3)	80	85	85	80
Thickness of Disc (cm)	0.32	0.33	0.33	0.32
Surface Area (cm^2)	8.042	8.042	8.042	8.042
Gradient (x E9)	7.44	7.72	6.06	8.27
Correlation	0.975	0.974	0.995	0.978
D Value (x E8)	2.37	2.69	2.11	2.63

Mean D Value	2.45 E -8
Standard Dev.	0.23 E -8

Table 3.31 Na diffusion coefficient of pfa 3

Time (seconds)	Sodium ion concentration			mols/l
	Disc A	Disc B	Disc C	Disc D
950 400	0.055	0.057	0.057	0.061
1 814 400	0.063	0.061	0.061	0.062
2 678 400	0.068	0.062	0.062	0.064
3 801 600	0.072	0.066	0.068	0.066
4 579 200	0.074	0.072	0.070	0.074

Volume of Cell (cm^3)	86	80	85	80
Thickness of Disc (cm)	0.34	0.33	0.33	0.33
Surface Area (cm^2)	8.042	8.042	8.042	8.042
Gradient (x E9)	3.98	3.58	3.58	3.98
Correlation	0.974	0.943	0.975	0.836
D Value (x E8)	1.45	1.18	1.25	1.31

Mean D Value	1.30 E -8
Standard Dev.	0.10 E -8

Table 3.32 Na diffusion coefficient of pfa 4

Time (seconds)	Sodium ion concentration			mols/l	
	Disc A	Disc B	Disc C	Disc D	Disc E
1 296 000	0.042	0.045	0.045	0.043	0.045
1 900 800	0.048	0.048	0.047	0.045	0.048
2 505 600	0.054	0.050	0.051	0.050	0.051
3 110 400	0.057	0.054	0.052	0.053	0.054
5 01 200	0.064	0.060	0.058	0.058	0.065
Volume of Cell (cm^3)	70	100	80	80	80
Thickness of Disc (cm)	0.32	0.32	0.32	0.33	0.32
Surface Area (cm^2)	8.042	8.042	8.042	8.042	8.042
Gradient (x E9)	5.38	2.69	2.69	5.38	5.38
Correlation	0.944	0.995	0.975	0.946	0.998
D Value (x E8)	1.50	1.07	0.86	1.77	1.71

Mean D Value	1.38 E -8
Standard Dev.	0.36 E -8

Table 3.33 Na diffusion coefficient of pfa 5

Time (seconds)	Sodium ion concentration		mols/l		
	Disc A	Disc B	Disc C	Disc D	Disc E
1 296 000	0.046	0.049	0.047	0.048	0.049
1 900 800	0.052	0.054	0.053	0.055	0.057
2 505 600	0.060	0.059	0.056	0.058	0.059
3 110 400	0.061	0.066	0.064	0.065	0.065
5 011 200	0.076	0.079	0.076	0.076	0.076
Volume of Cell (cm^3)	80	80	80	80	80
Thickness of Disc (cm)	0.33	0.33	0.32	0.33	0.33
Surface Area (cm^2)	8.042	8.042	8.042	8.042	8.042
Gradient (x E9)	8.07	8.17	8.07	8.07	8.07
Correlation	0.976	0.993	0.986	0.981	0.985
D Value (x E8)	2.65	2.68	2.57	2.65	2.65

Mean D Value	7.64 E -8
Standard Dev.	0.04 E -8

APPENDIX 4

Adjustment and Comparison of Previously Reported OH Concentrations

Adjustment Method

Specimens were compared at a common water cement ratio of 0.5. Specimens which were originally made using another water cement ratio were adjusted using the calculation shown below. No account was taken of changes in concentration due to age.

$$\frac{\text{WC (Original)}}{0.5} \times \text{OH Concentration} = \text{Adjusted OH Concentration}$$

Table 4.1

Author	Key*	Age	W/C	Cement (Eq Na_2O %)	Recorded OH (mmols/l)	Adjusted OH (mmols/l)
Diamond(106)	D	30	0.4	0.71	570	456
Glasser, Marr(38)	G	90	0.6	0.50	270	324
				0.95	590	708
Holden, Page, Short(108)	H	84	0.5	0.54	347	347
				0.71	589	589
				0.86	479	479
Kollek et al (105)	K	30	0.5	0.34	300 (M)	300
				0.68	500 (M)	500
				0.92	630 (M)	630
Longuet(104)	L	28	0.5	0.85	698	698
				0.99	685	685
				1.04	717	717
Page, Venneslånd (37)	P	28	0.5	1.19	834	834

(M) Mortar of aggregate cement ratio of 2.25:1

* Key used to label Figures 4.1 and 4.2.

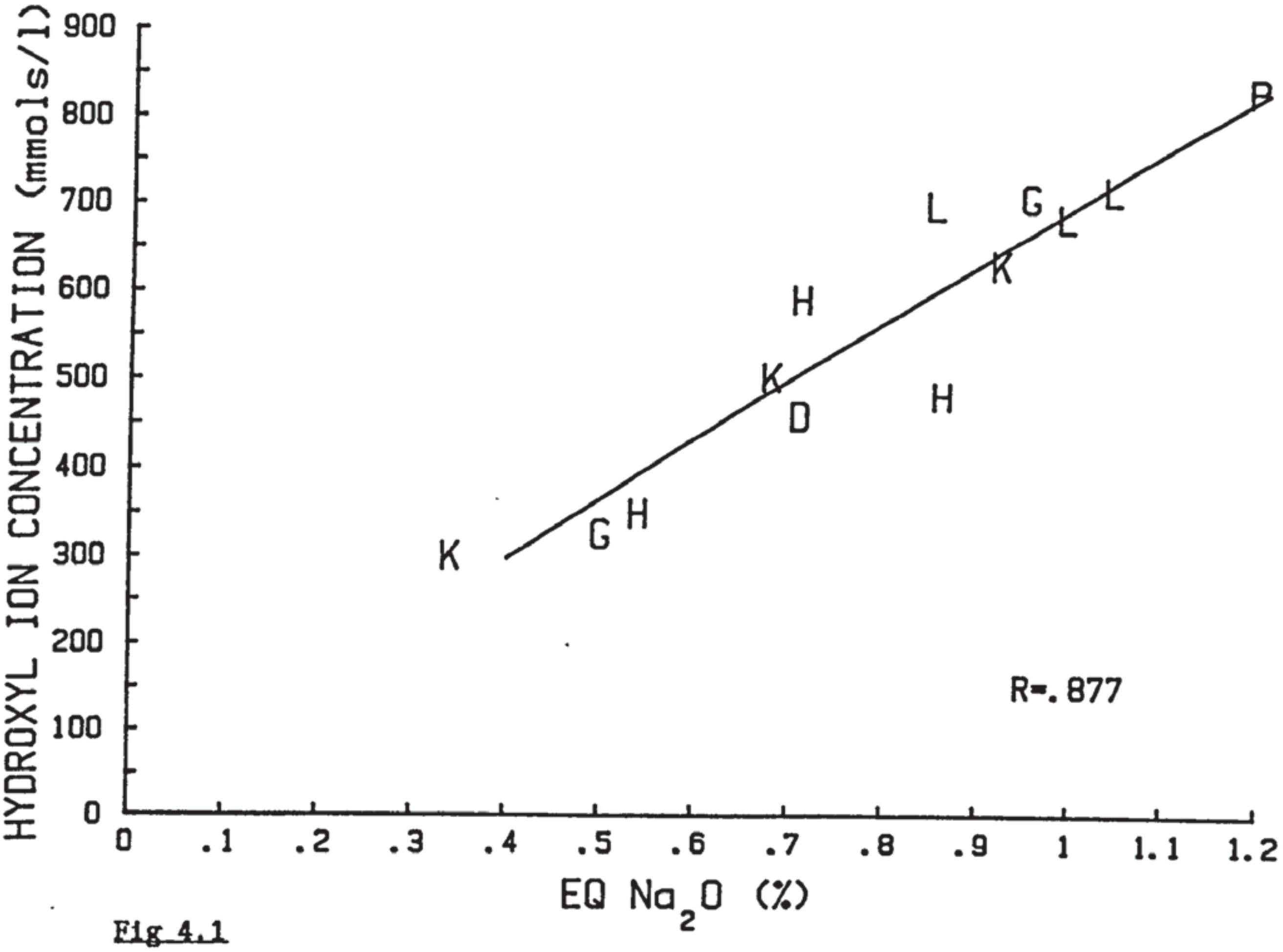


Fig 4.1

Pore solution OH concentration reported by previous workers (corrected)

Ditto including results of this work.

Fig 4.2

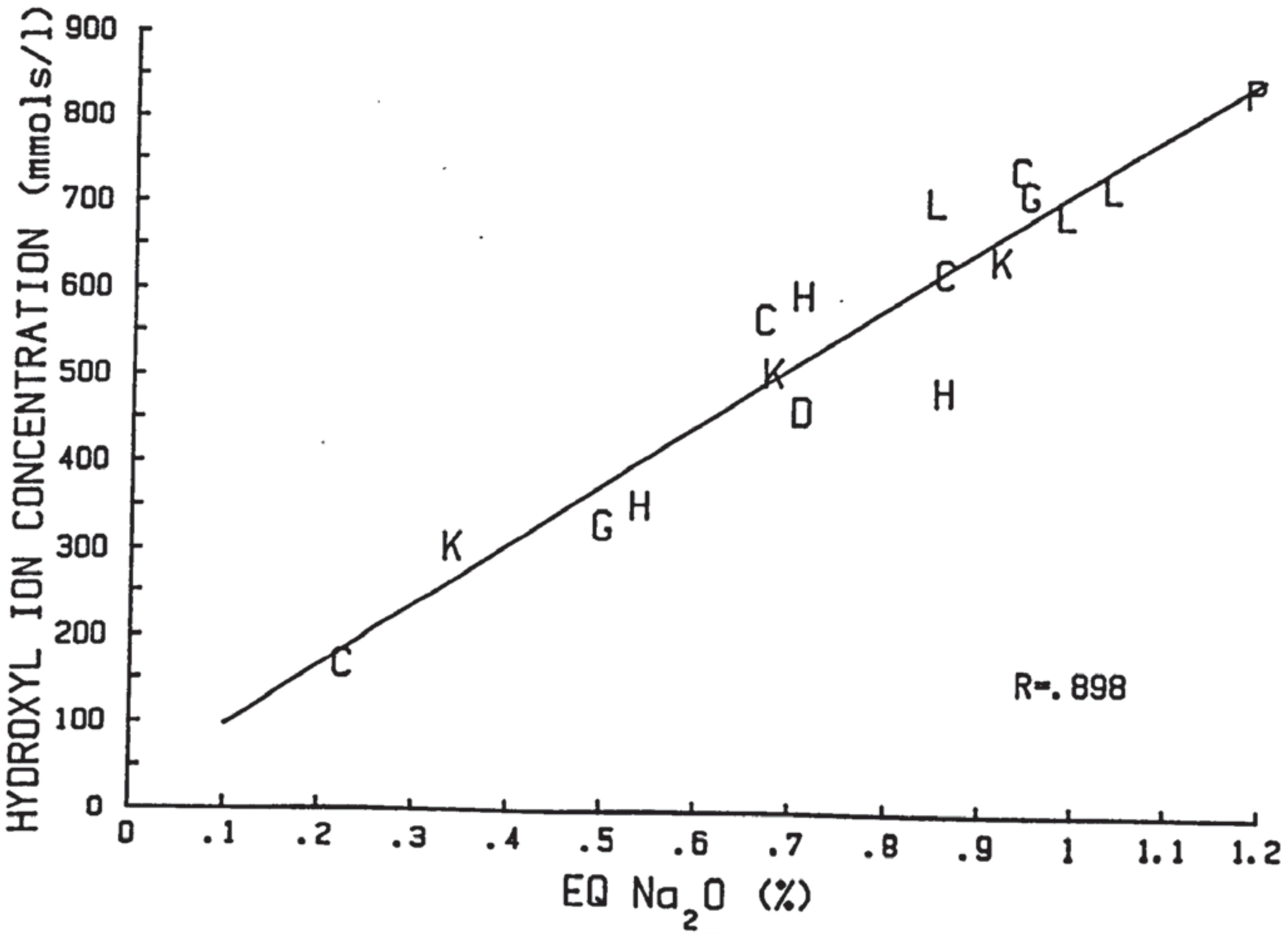


TABLE 4.2 CEMENT PASTE SPECIMENS: THE INFLUENCE OF TIME AND ALKALI CONTENT

PASTE (eq.Na_2O)	AGE	IONIC CONCENTRATIONS mmols/l				We g/g	COR. CONC mmols/l			QTY OF IONS IN SOLN mmols/g		
		OH	pH	K	Na		OH	K	Na	OH	K	Na
Cement	7	161	13,21	85	69	0,329	106	56	45	53	28	23
A	28	166	13,22	96	71	0,322	107	62	46	54	31	23
(0,225%)	84	205	13,30	105	87	0,320	131	67	56	66	34	28
	365	200	13,30	102	90	0,315	126	64	57	63	32	29
Cement	7	529	13,72	454	58	0,320	339	291	37	170	146	19
B	28	562	13,75	467	77	0,301	338	281	46	169	141	23
(0,67%)	84	581	13,76	475	106	0,300	349	285	64	175	143	32
	365	542	13,73	418	76	0,294	319	246	47	160	123	24
Cement	7	588	13,77	455	97	0,349	410	318	68	205	159	34
C	28	615	13,79	500	109	0,330	406	330	72	203	165	36
(0,86%)	84	650	13,81	546	117	0,310	403	339	73	202	170	37
	365	615	13,79	485	125	0,300	369	291	75	185	146	38
Cement	7	688	13,84	502	180	0,349	480	350	126	240	175	63
D	28	737	13,87	516	213	0,330	486	341	141	243	171	71
(0,94%)	84	775	13,89	543	235	0,320	496	348	150	248	174	75
	365	709	13,85	470	231	0,311	441	392	144	221	146	72

TABLE 4.3 CEMENT MORTAR SPECIMENS : THE INFLUENCE OF TIME AND ALKALI CONTENT

MORTARS (eq.Na₂O)	AGE	IONIC CONCENTRATION mmols/l				We g/g	COR. CONC mmols/l			QTY OF IONS IN SOLN mmols/g		
		OH	pH	K	Na		OH	K	Na	OH	K	Na
Cement A (0,225%)	7	132	13,12	67	64	0,333	88	45	43	44	23	22
	28	148	13,17	77	65	0,329	97	51	43	49	26	22
	84	162	13,21	88	75	0,321	104	56	48	52	28	24
	365	153	13,18	80	74	0,319	98	51	47	49	26	24
Cement B (0,67%)	7	468	13,67	390	77	0,340	318	265	52	159	133	26
	28	490	13,69	406	81	0,336	329	273	54	165	137	27
	84	490	13,69	415	78	0,333	326	276	52	163	138	26
	365	435	13,64	360	78	0,331	288	238	52	144	119	26
Cement C (0,86%)	7	550	13,74	447	102	0,312	343	279	64	172	140	32
	28	560	13,75	453	105	0,304	340	275	64	170	138	32
	84	575	13,76	462	111	0,295	339	272	65	170	136	33
	365	513	13,71	396	114	0,293	301	232	67	151	116	34
Cement D (0,94%)	7	575	13,76	400	171	0,330	380	264	113	190	132	57
	28	643	13,81	468	173	0,323	415	302	112	208	151	56
	84	631	13,80	434	195	0,316	399	274	123	200	137	62
	365	553	13,74	368	190	0,313	346	230	119	173	115	59

TABLE 4.4 THE INFLUENCE OF AGGREGATE ON THE POTASSIUM RATIO TO SODIUM IONS IN SOLUTION

CEMENT Total ions m/g	Age days	K/Na Pastes	K/Na Mortars	Δ ION DUE TO AGGREGATE			
				K mmols	Na mmols	K %	Na%
		0.88	0.88				
A	7	1,22	1,05	-5	-1	-18	-4
	28	1,35	1,18	-5	-1	-16	-4
K = 0,068	84	1,28	1,17	-6	-4	-18	-14
Na = 0,077	365	1,10	1,08	-6	-5	-19	-17
		5.1	5.1				
B	7	7,68	5,12	-13	+7	-9	+37
	28	6,13	5,07	-4	+4	-3	+17
K = 0,357	84	4,47	5,31	-5	-6	-3	-19
Na = 0,07	365	5,13	4,58	-4	-6	-3	-25
		3.11	3.11				
C	7	4,68	4,38	-19	-2	-12	-6
	28	4,58	4,31	-27	-4	-16	-11
K = 0,421	84	4,59	4,12	-34	-4	-20	-11
Na = 0,135	365	3,84	3,41	-30	-4	-21	-11
		1.92	1.92				
D	7	2,78	2,37	-43	-6	-25	-10
	28	2,41	2,70	-20	-15	-12	-17
K = 0,409	84	2,32	2,21	-37	-13	-21	-17
Na = 0,213	365	2,72	1,95	-81	-13	-41	-18

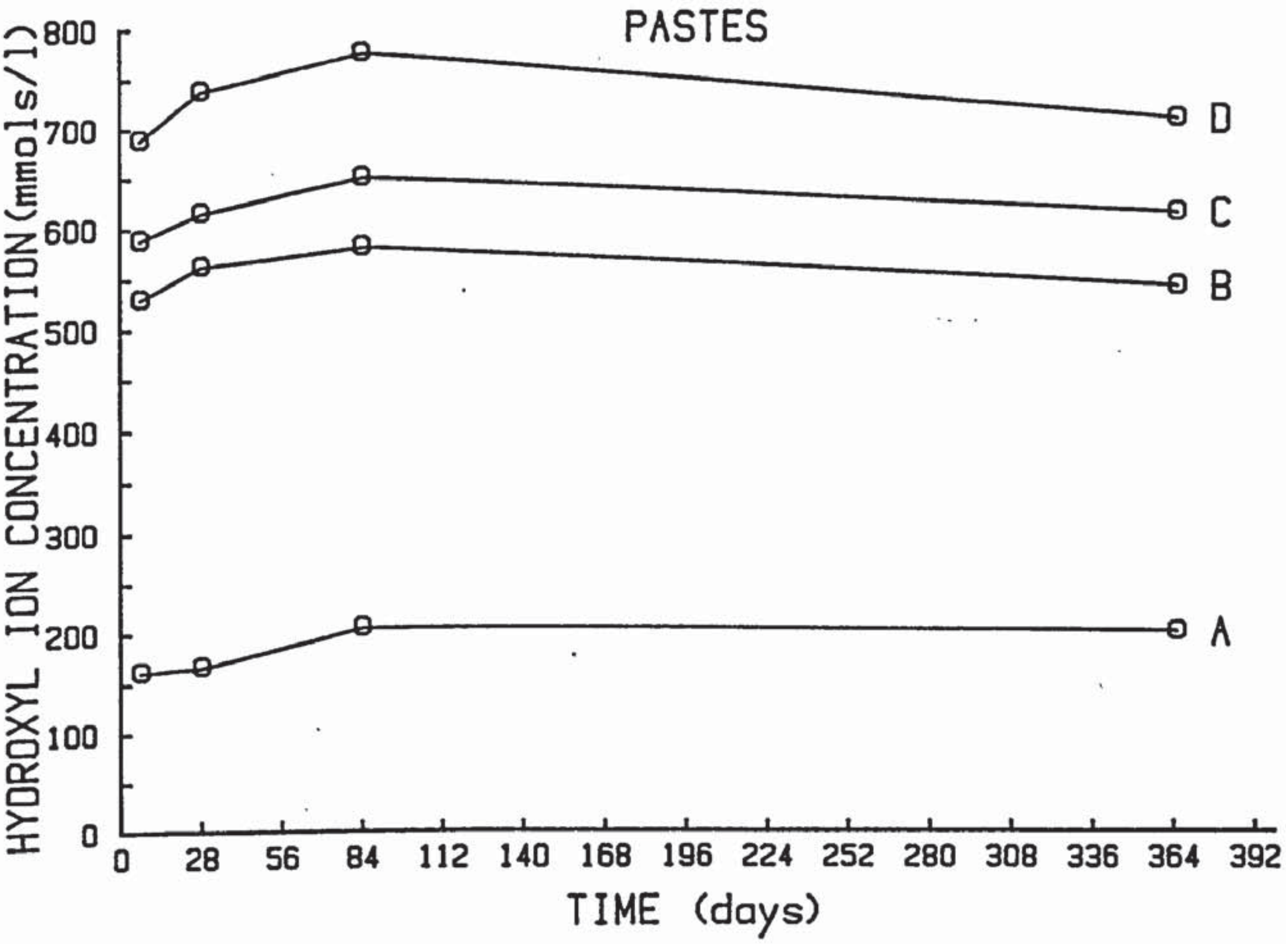
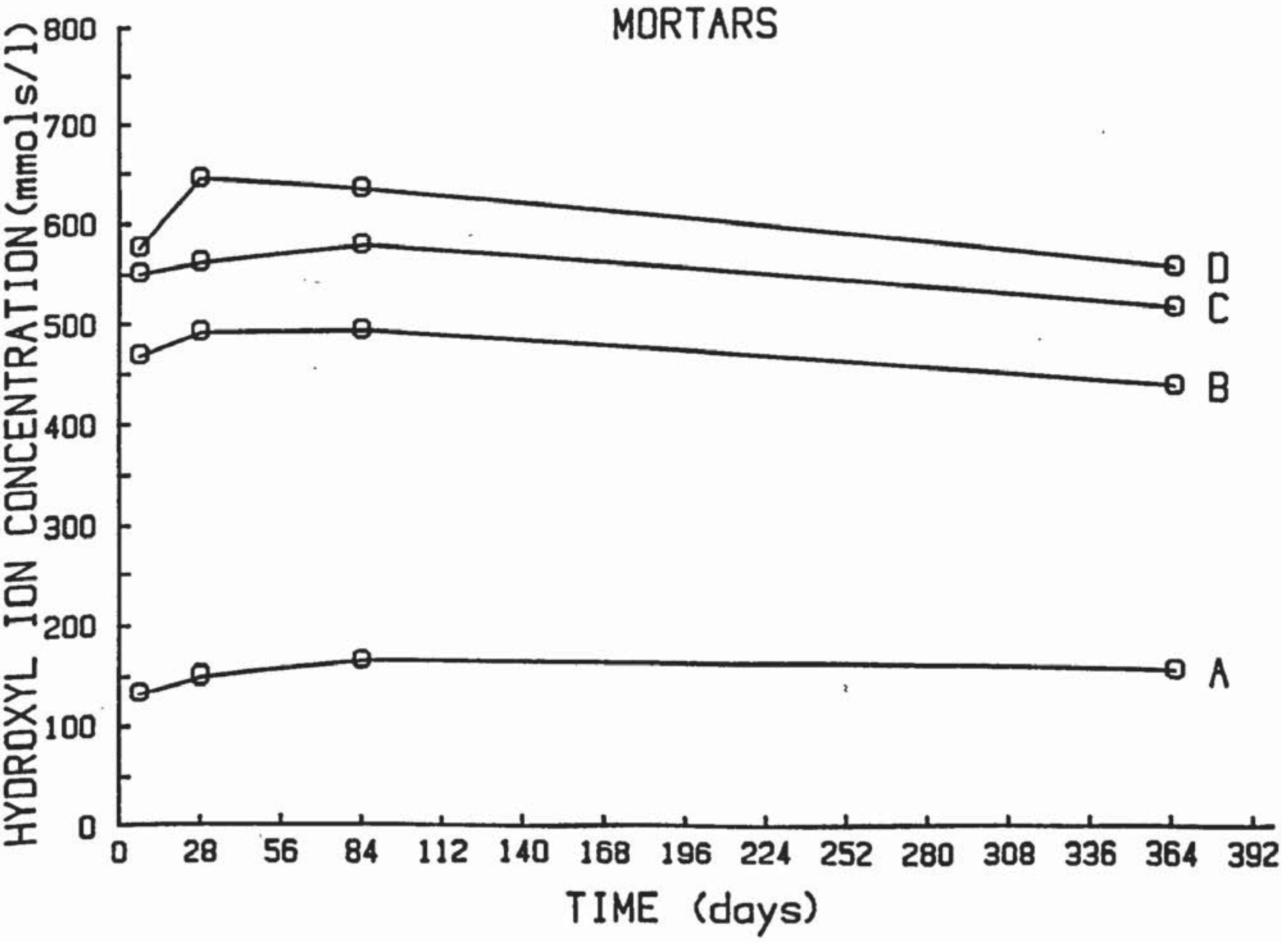


Fig 4.3 OH ion concentration of cement paste specimens as a function of time.

Fig 4.4 OH ion concentration of cement mortar specimens as a function of time.



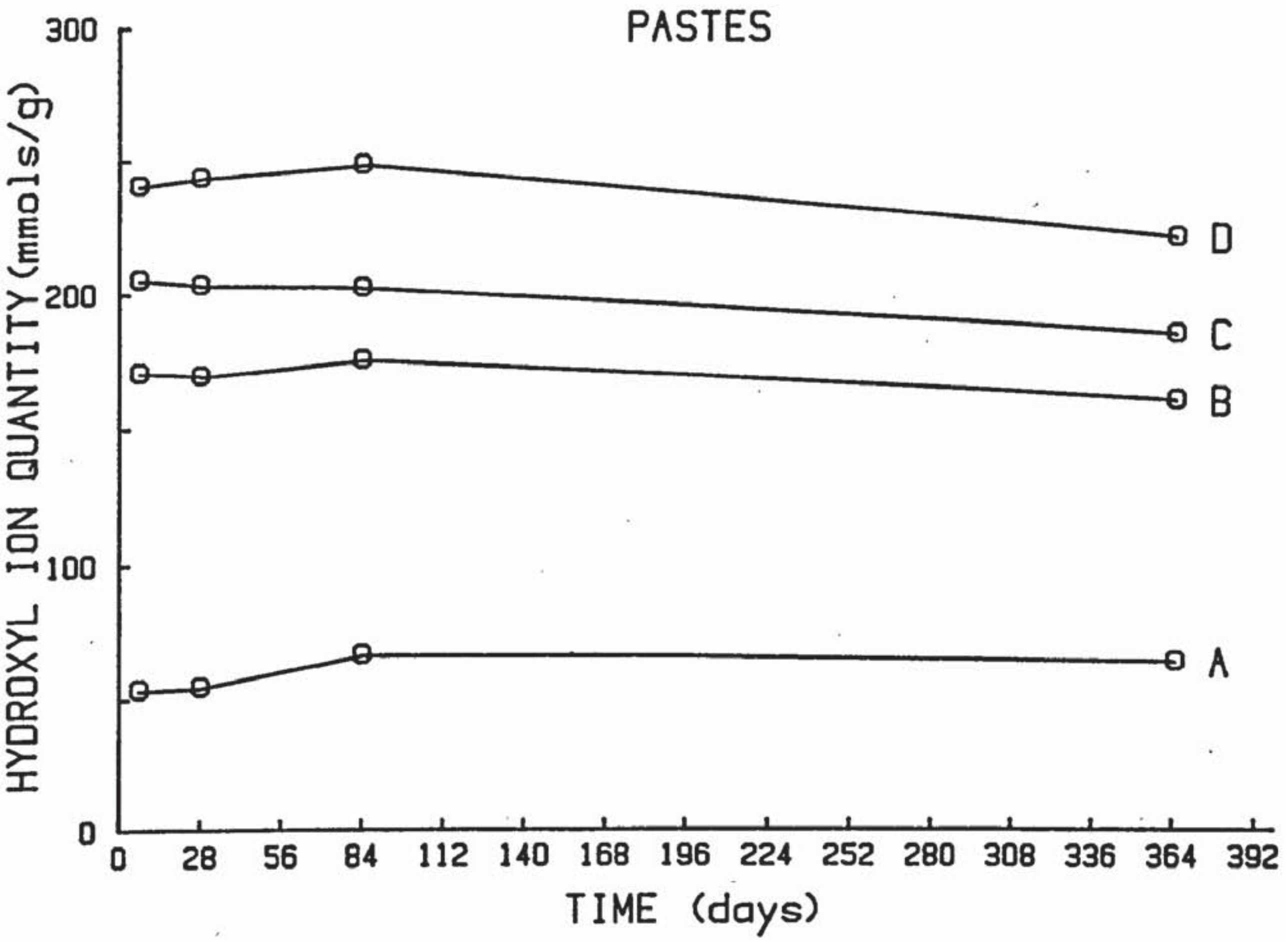
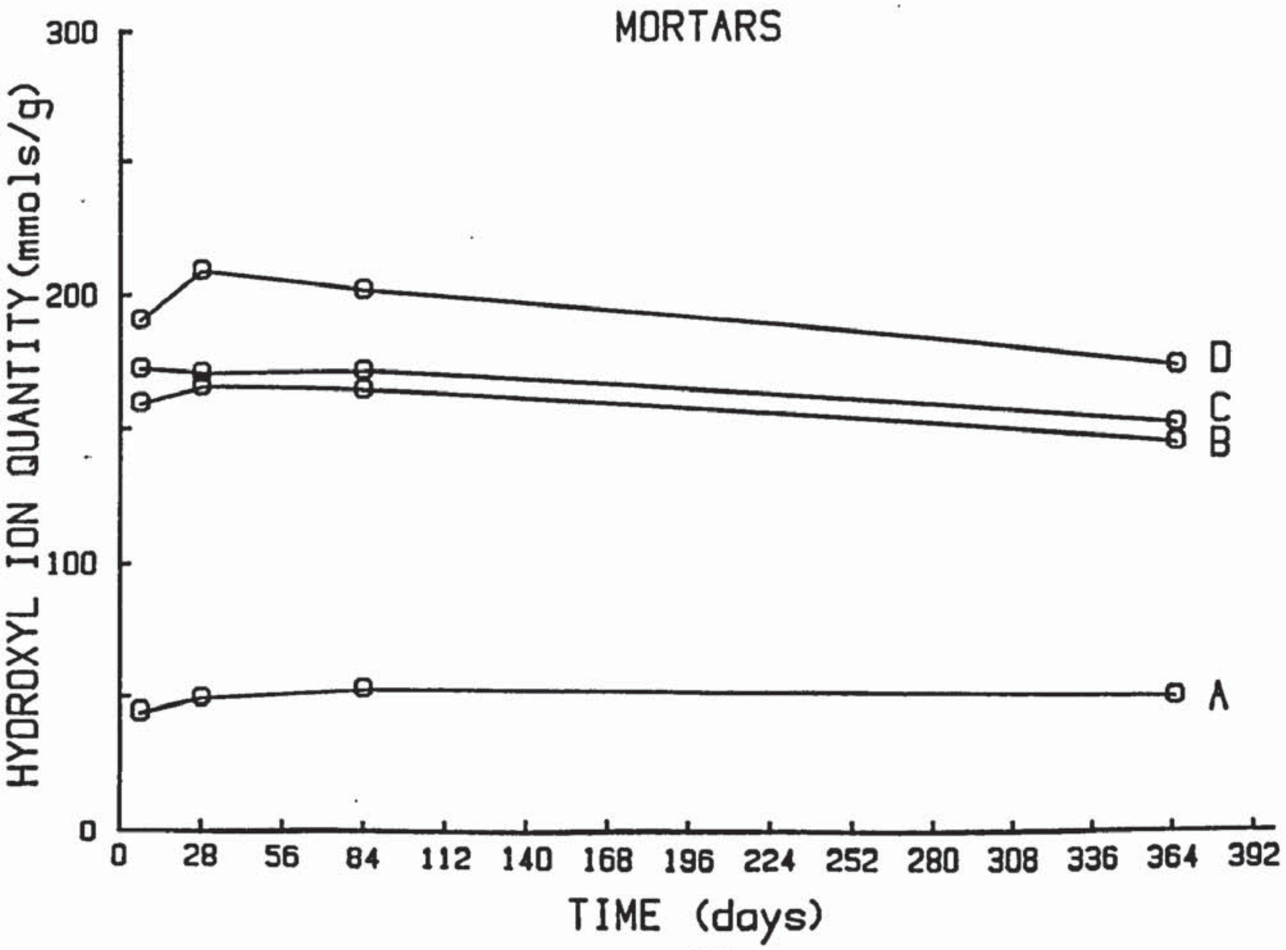


Fig 4.5 Quantity of OH ions in solution (mmols/) as a function of time

Fig 4.6 Quantity of OH ions in solution (mmols/) as a function of time



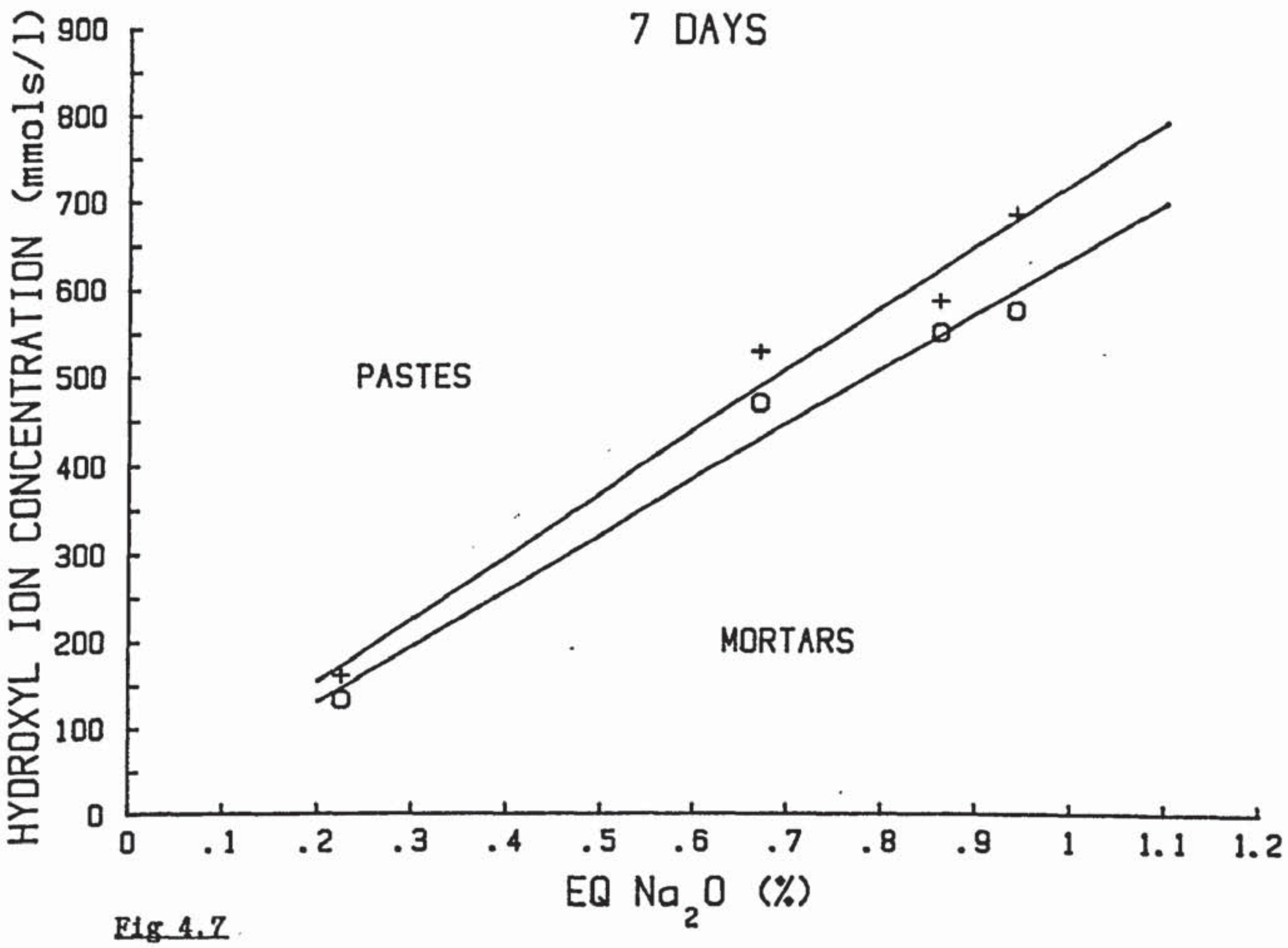
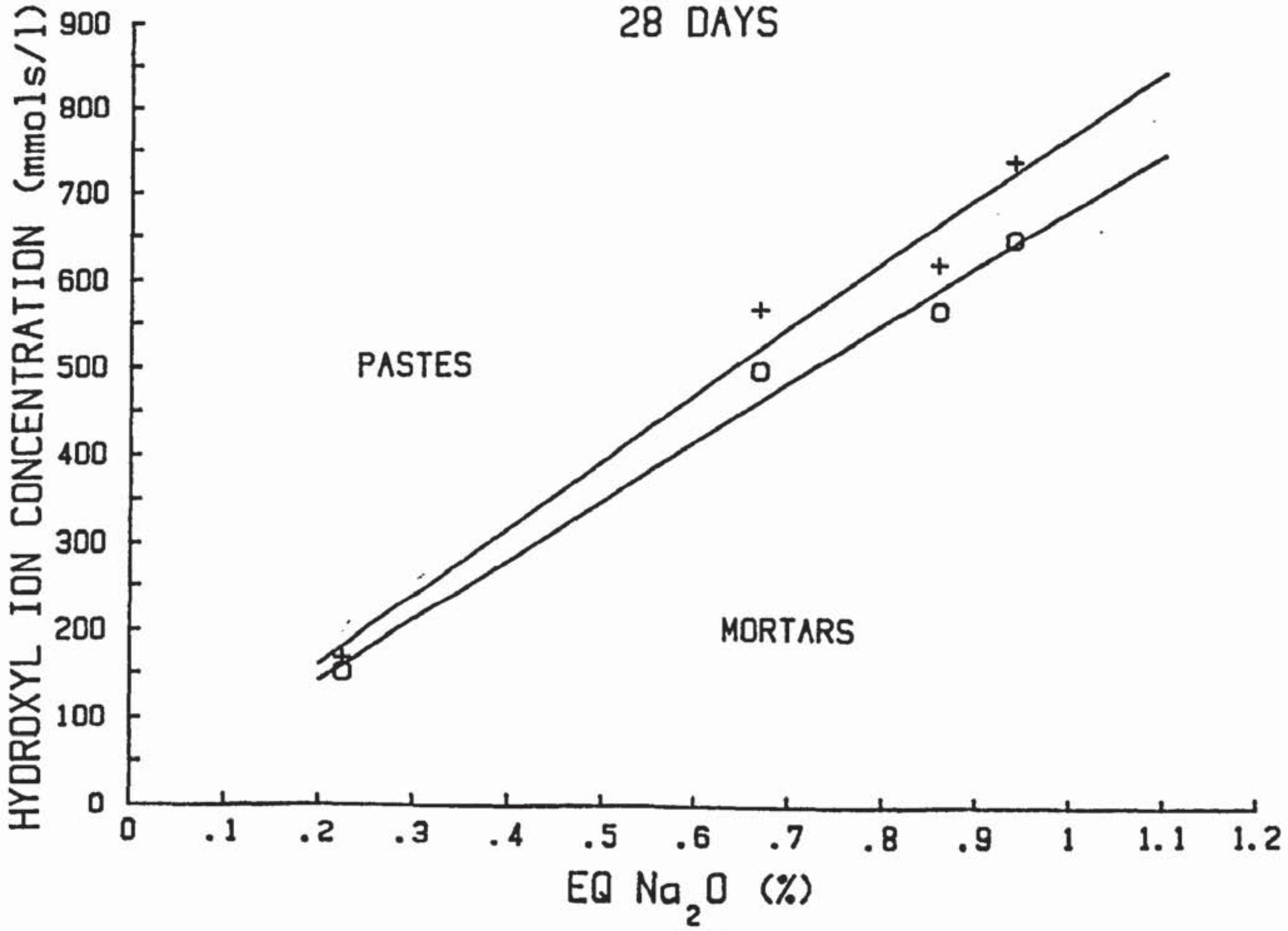


Fig 4.7

Hydroxyl ion concentration difference between cement pastes and mortars

Fig 4.8



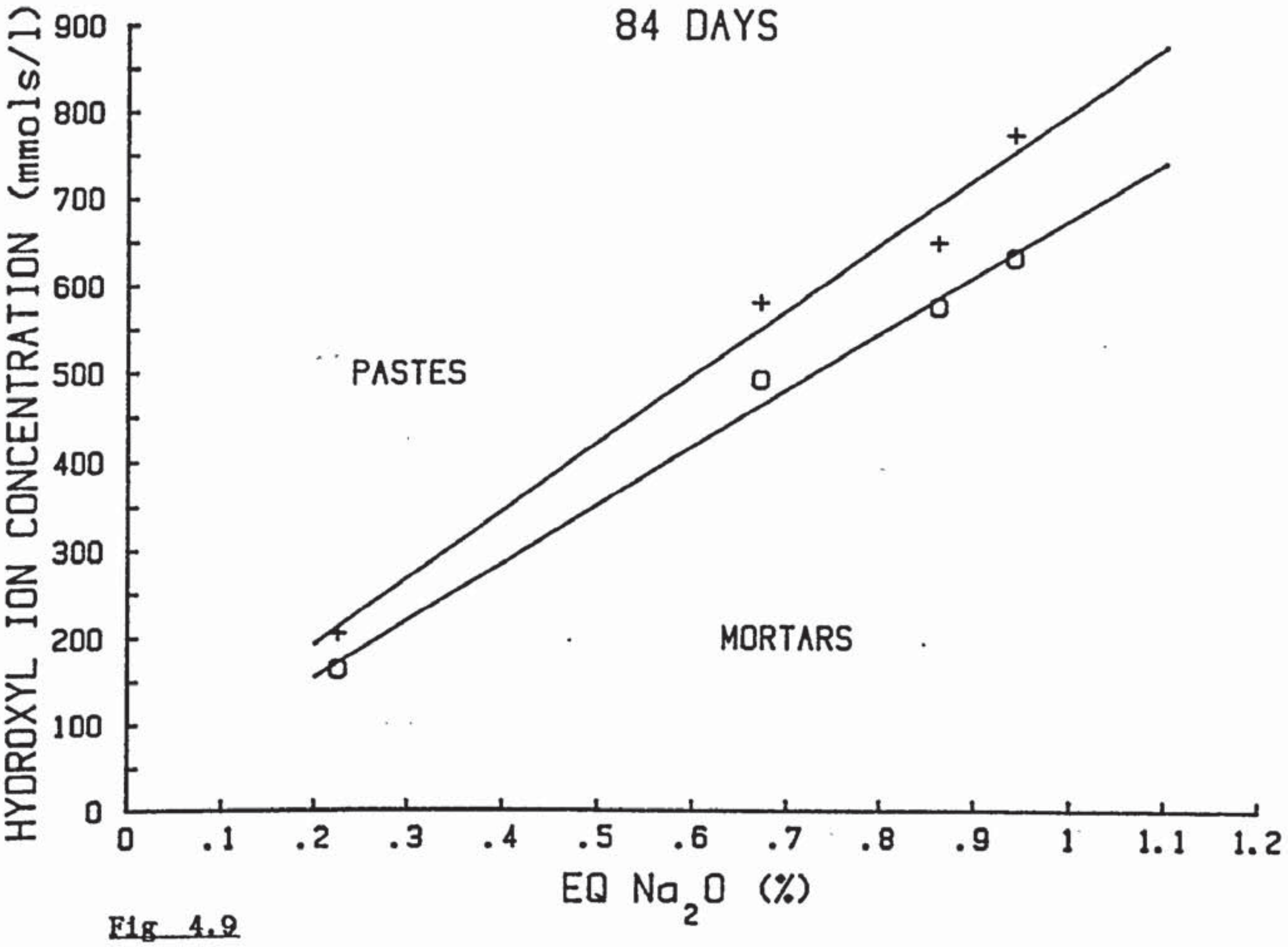
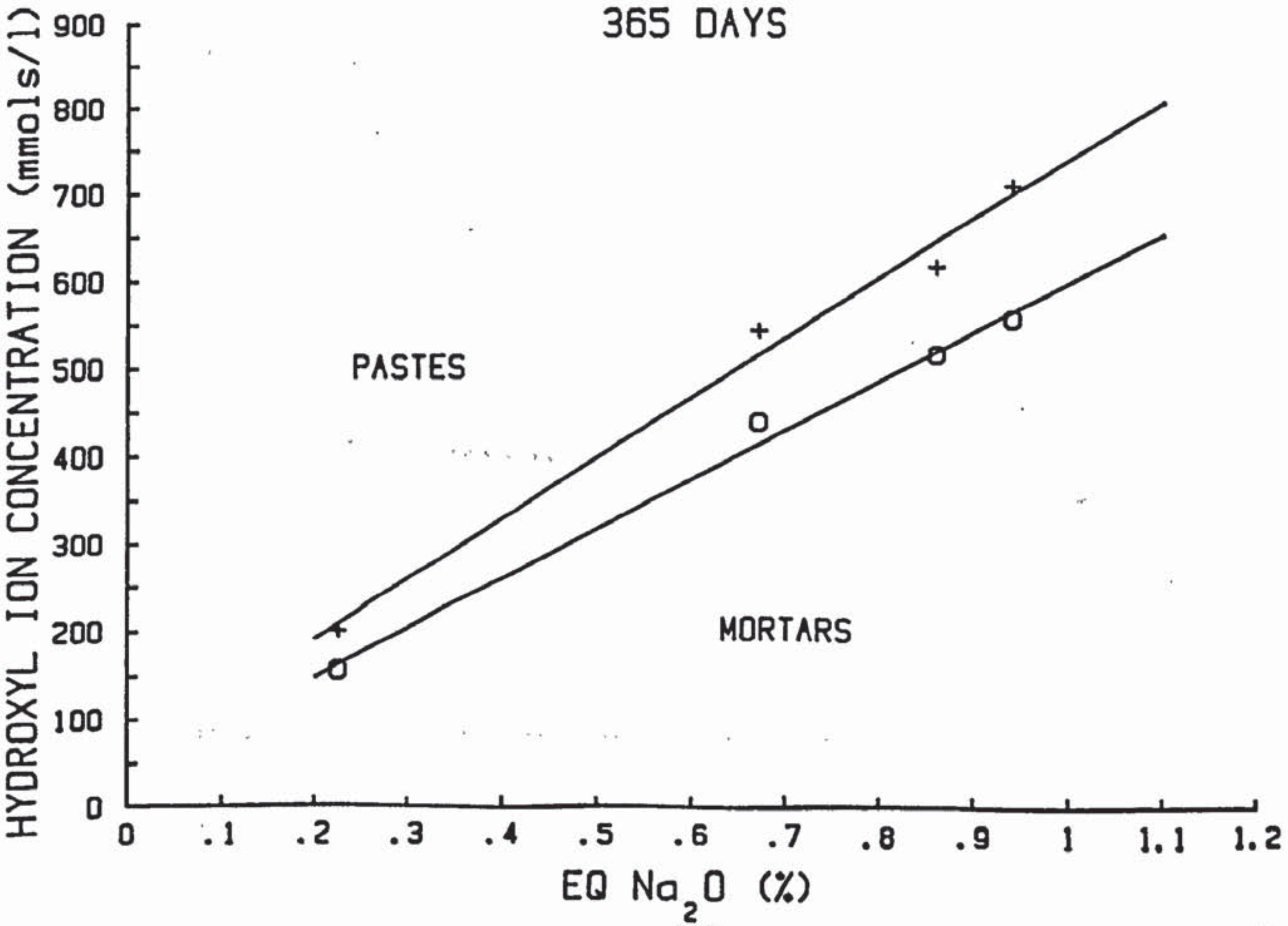


Fig 4.9

Hydroxyl ion concentration difference between cement pastes and mortars

Fig 4.10



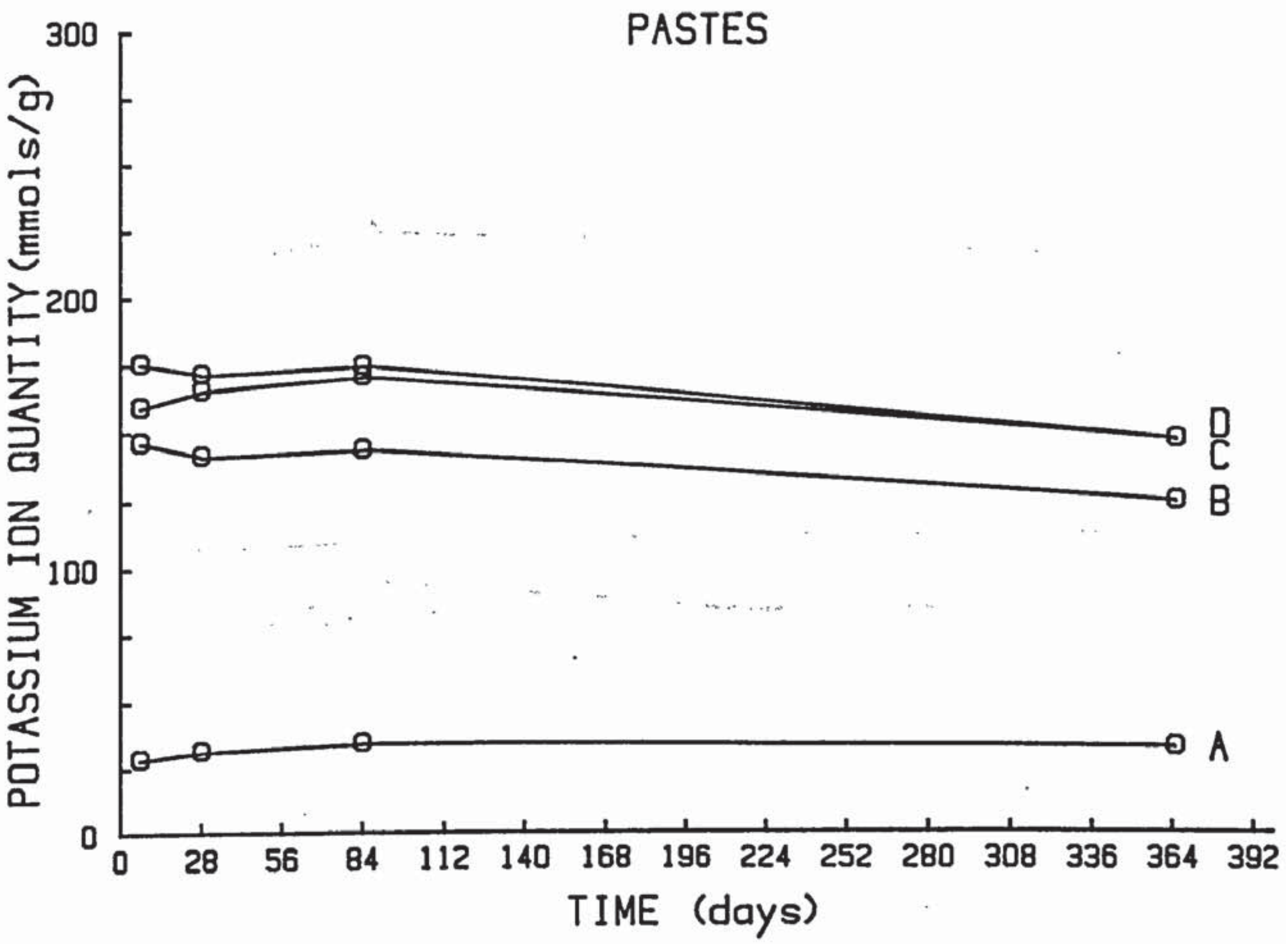
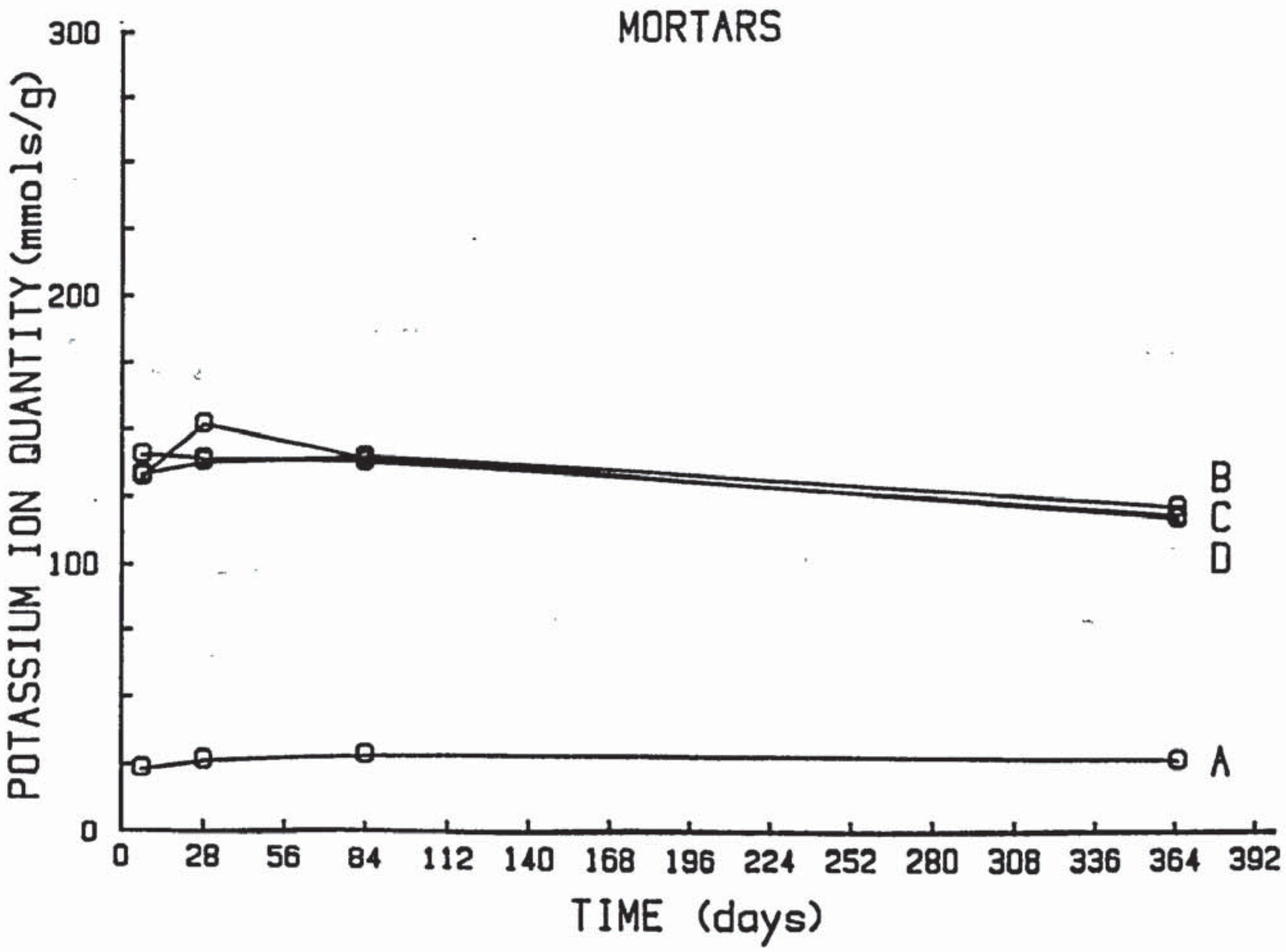


Fig 4.11

Quantity of potassium ions in solution as a function of time

Fig 4.12



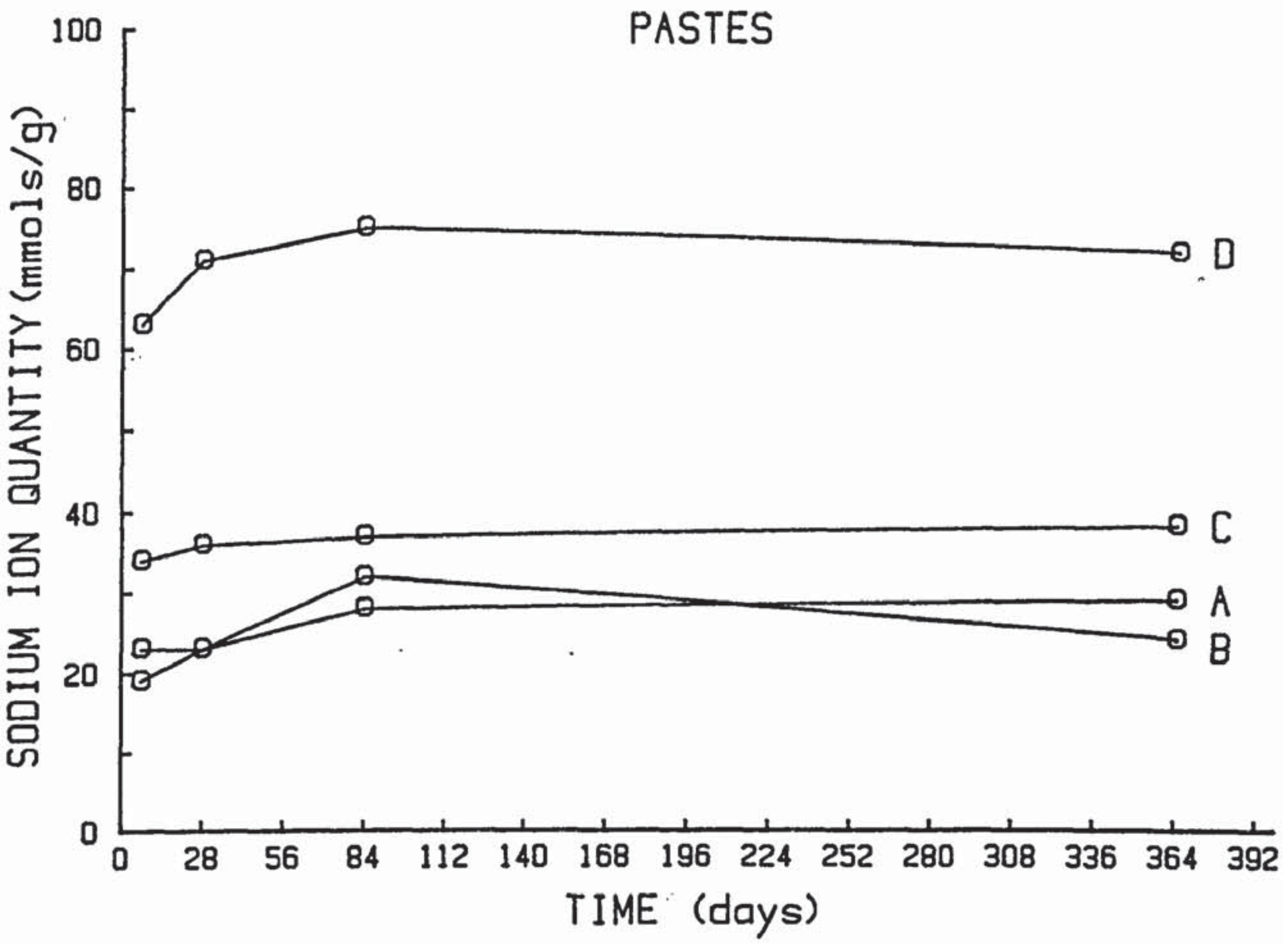
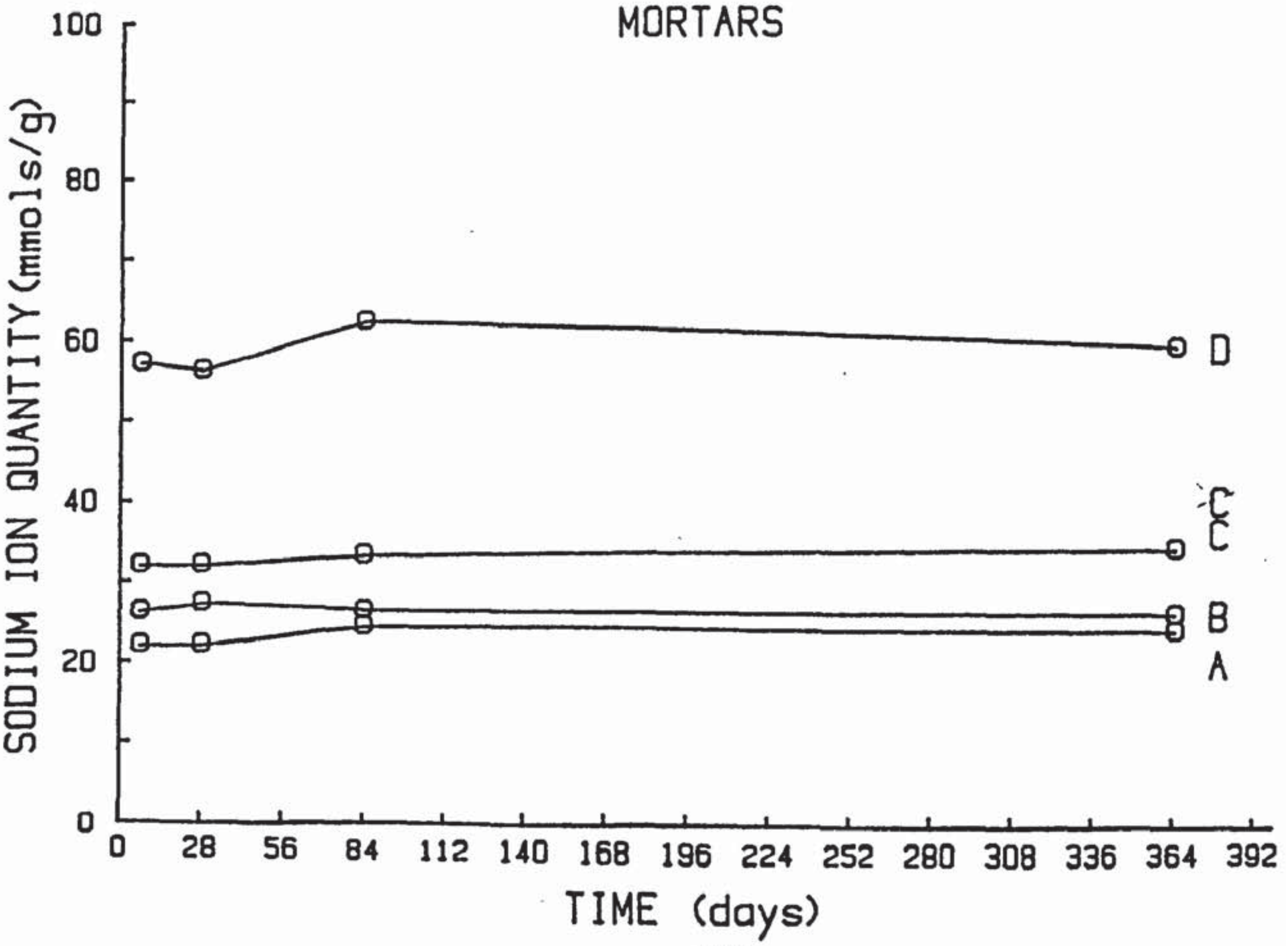


Fig 4.13

Quantity of Na ions in solution as a function of time

Fig 4.14



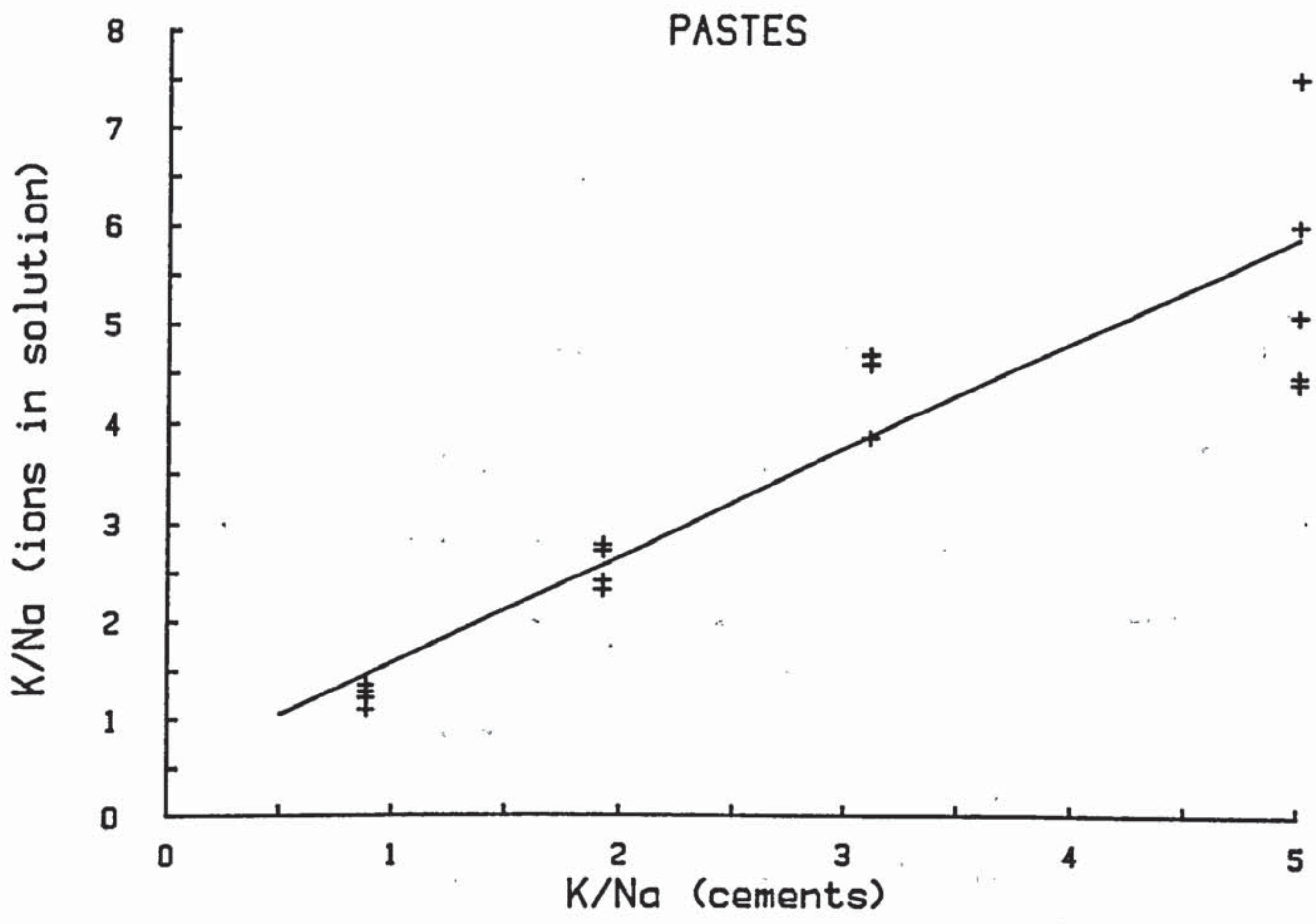


Fig 4.15

Ratio of Potassium to Sodium in solution for cement pastes

Ratio of Potassium to Sodium in solution for cement mortars

Fig 4.16

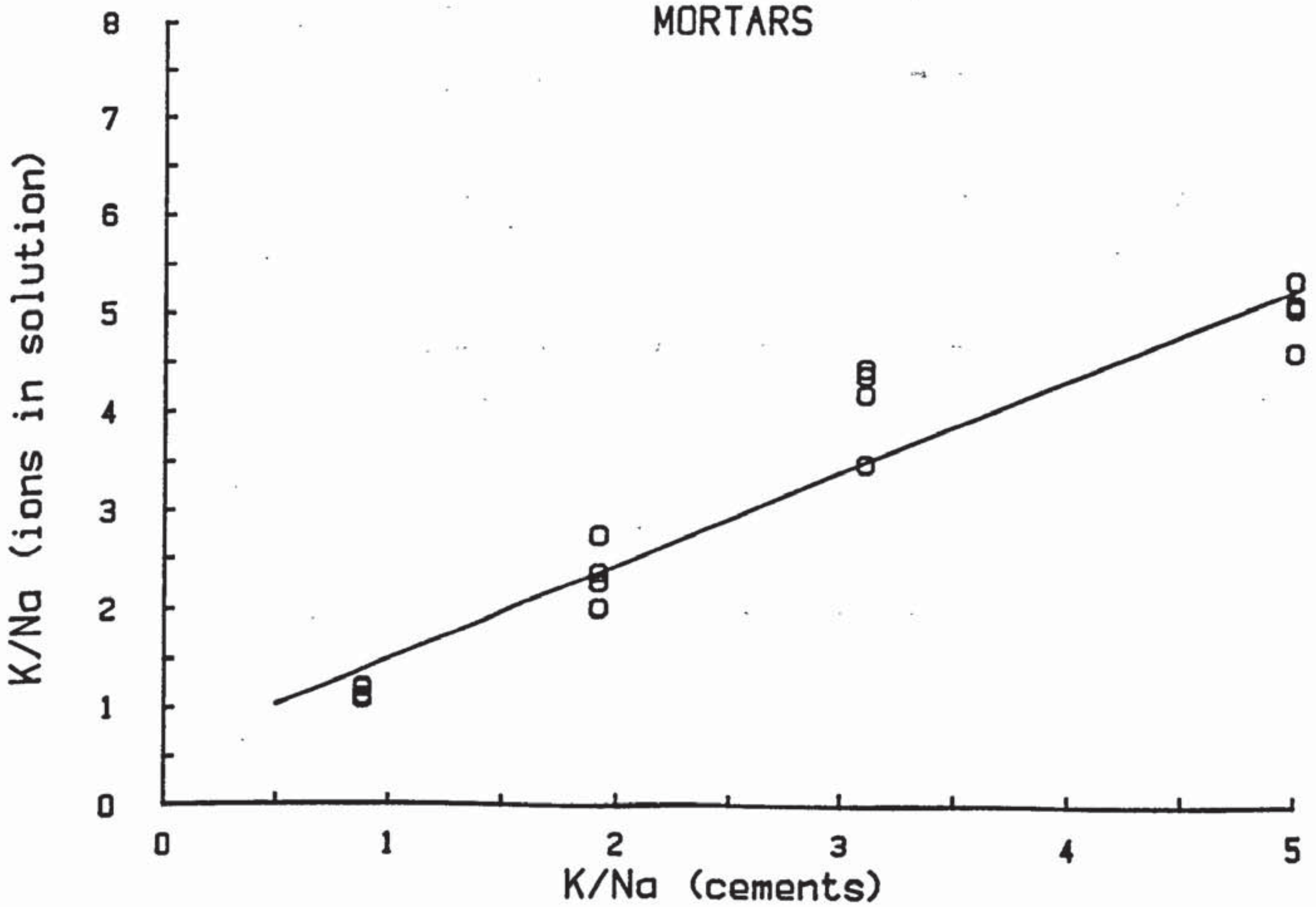


TABLE 4.5 CONCRETE SPECIMENS : THE INFLUENCE OF TOTAL ALKALI CONTENT

CONCRETE	Na$_2$O kg/m^3	IONIC CONCENTRATIONS mmols/l				We g/g	QTY OF IONS IN SOLN mmols/g			QTY OF IONS IN SOLN x 10^3 mols/m^3		
		OH	pH	K	Na		OH	K	Na	OH	K	Na
CEMENT A	2	157	13,20	76	69	0,344	55	26	24	49	23	21
	3	173	13,24	87	79	0,314	54	28	25	72	37	33
	4	166	13,22	82	75	0,306	52	26	23	92	46	41
	5	177	13,25	89	79	0,245	44	22	20	98	49	44
CEMENT B	2											
	3	346	13,54	299	54	0,278	96	83	15	35	30	5
	4	447	13,65	353	83	0,218	98	77	18	44	34	8
	5	457	13,66	385	78	0,186	85	72	15	51	43	9
CEMENT C	2											
	3	436	13,64	364	58	0,247	108	90	15	45	31	3
	4	512	13,71	423	86	0,211	108	89	18	50	41	8
	5	525	13,72	443	87	0,175	92	78	15	53	45	9
CEMENT D	2											
	3	575	13,76	407	172	0,244	140	100	42	45	32	13
	4	631	13,80	442	184	0,202	127	90	37	54	38	16
	5	646	13,81	460	193	0,175	113	81	34	60	43	18

TABLE 4,6 CEMENT CONTENT AND AGGREGATE CEMENT RATIO OF CONCRETES

Total Alkali Content of Concrete Eq. Na_2O								
Eq.Na_2O	2 Kg/m³		3 Kg/m³		4 Kg/m³		5 Kg/m³	
CEMENT	CC	AC	CC	AC	CC	AC	CC	AC
A	888	1,1	1333	0,3	1777	0	2222	0
B	364	4,9	448	3,7	597	2,4	746	1,7
C	233	8,6	349	5,2	465	3,6	581	2,5
D	213	9,5	319	5,9	425	4,4	531	2,9

CC Cement Content Kg/m³
AC Aggregate Cement ratio

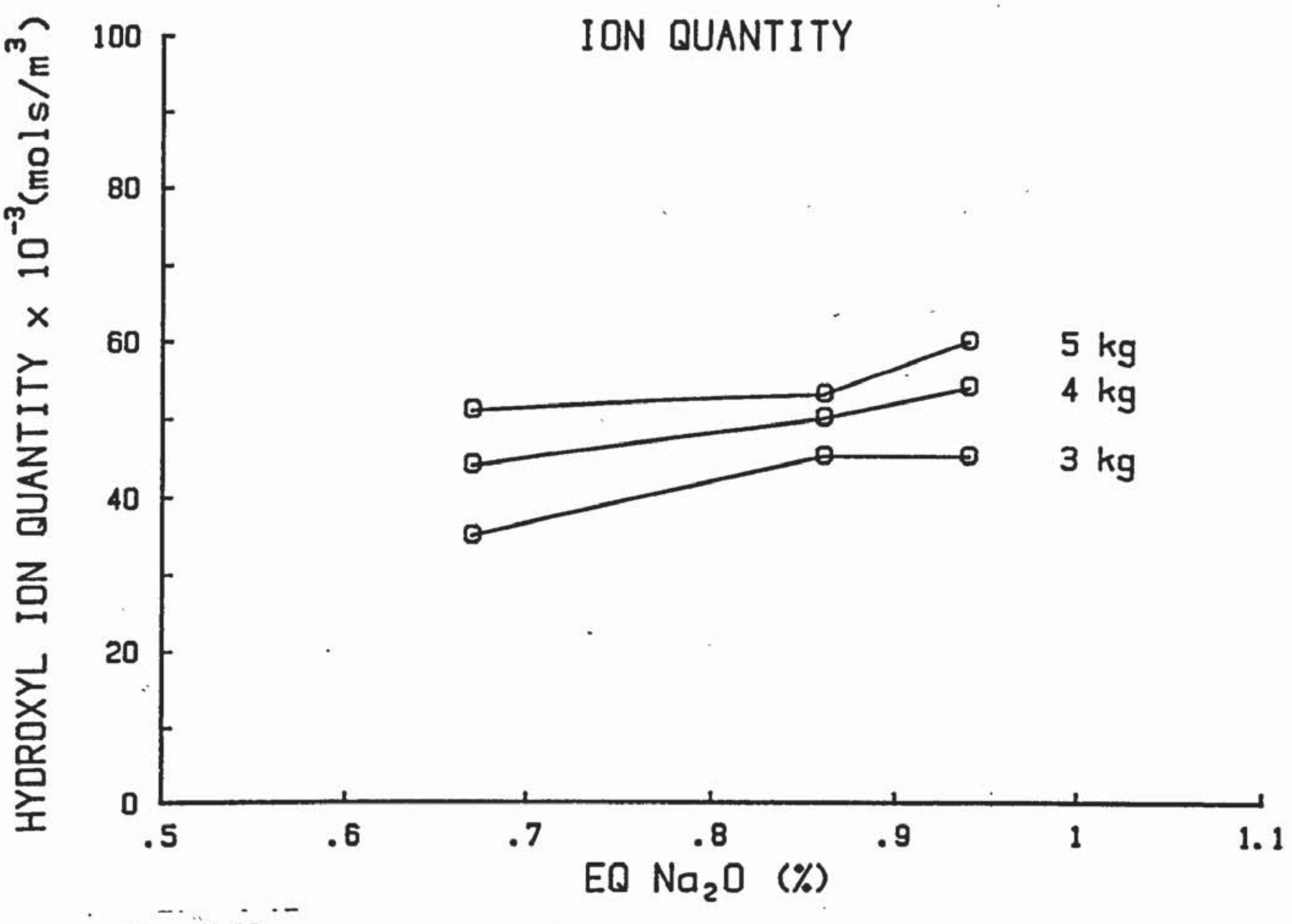
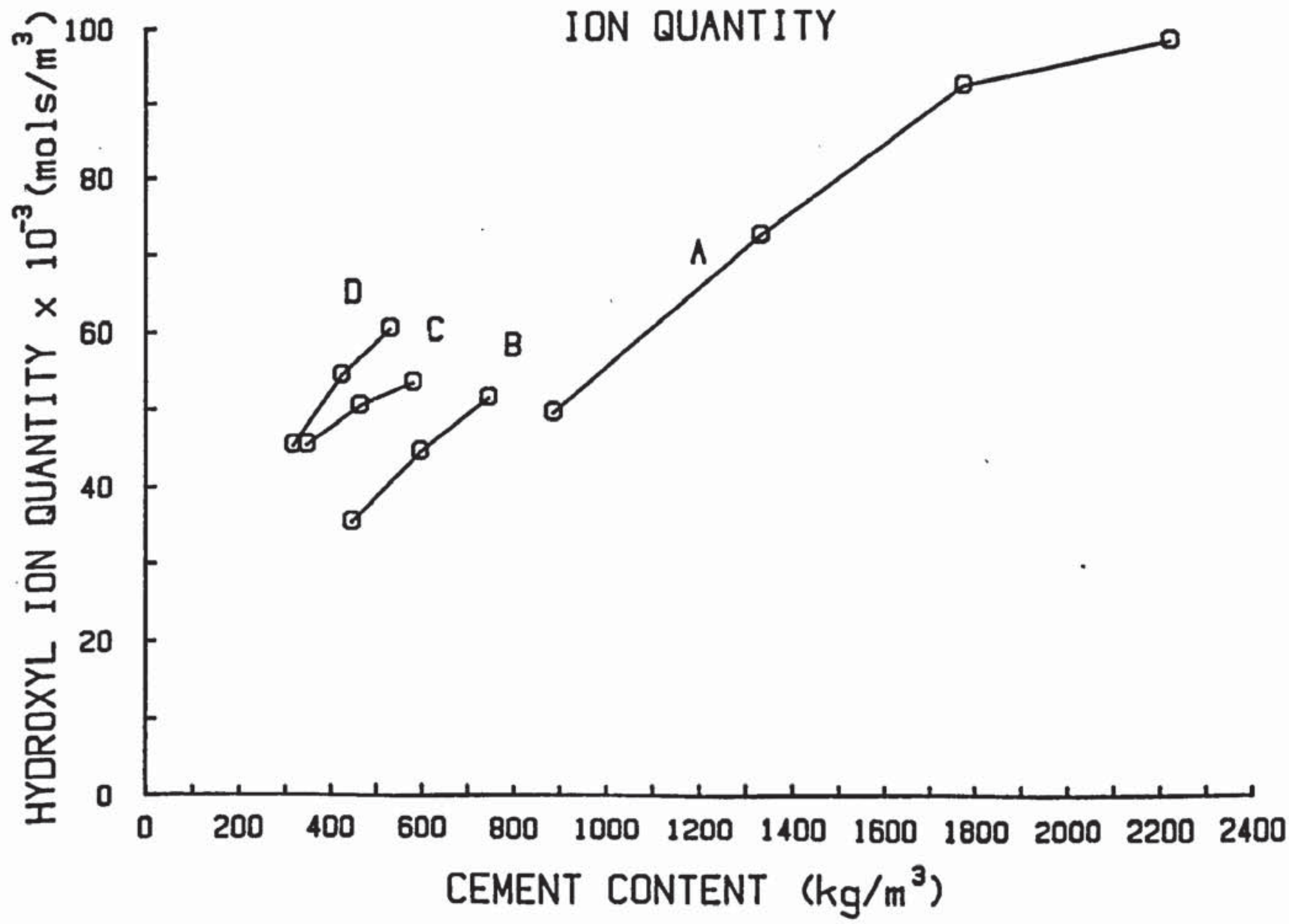


Fig 4.19

OH ion quantity as a function of cement alkali content

OH ion quantity as a function of cement content per cubic metre concrete

Fig 4.20



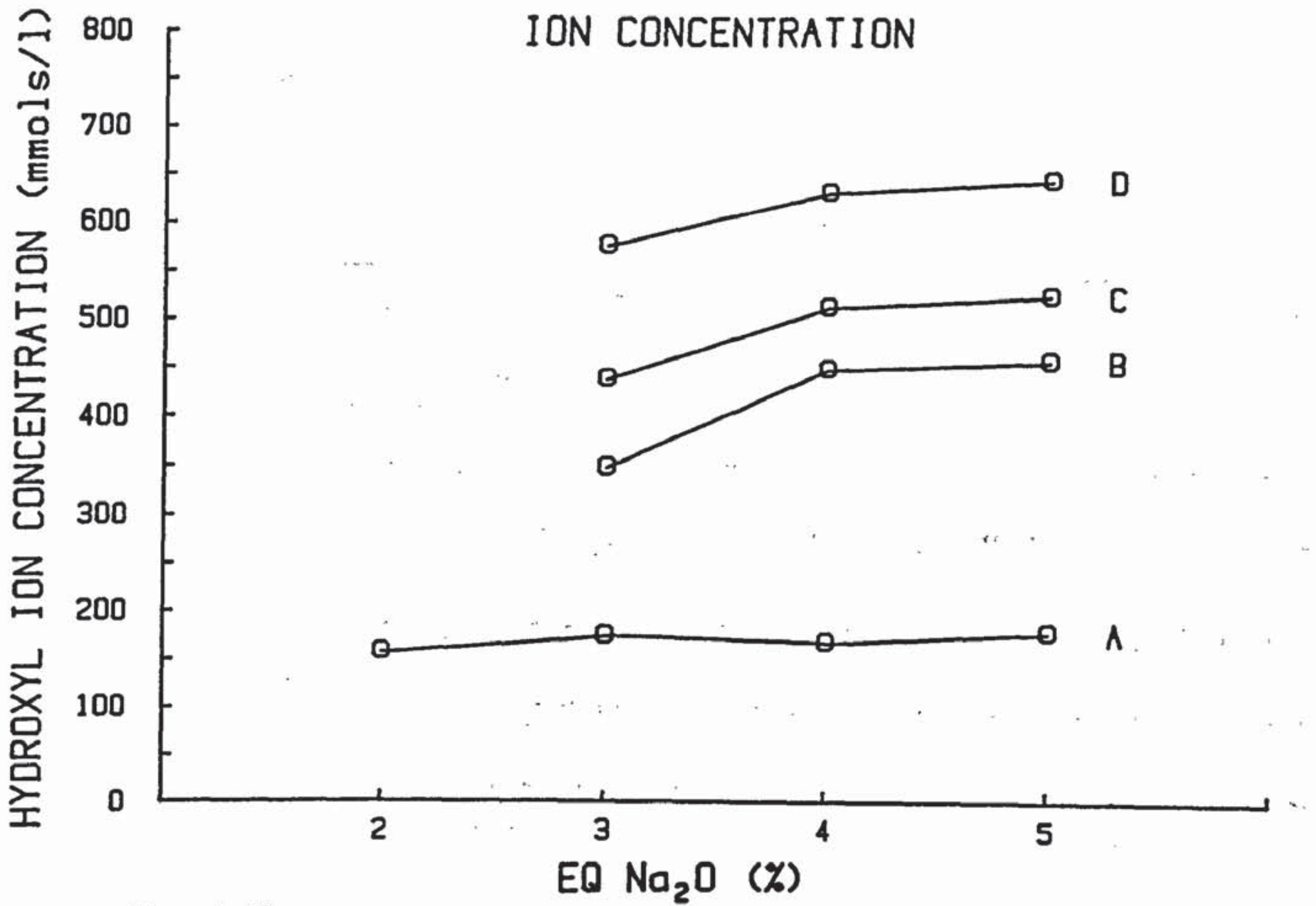
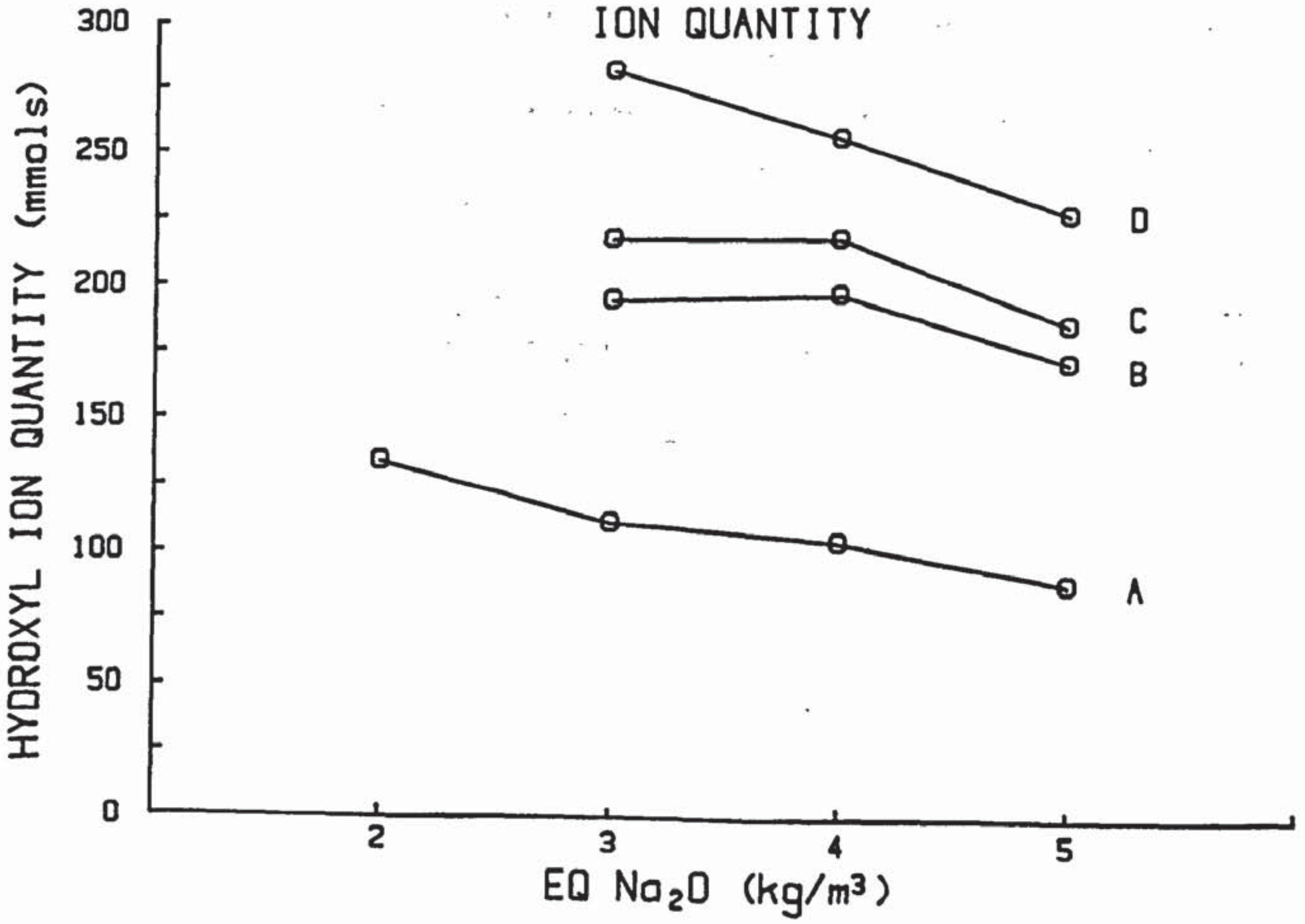


Fig 4.17

OH ion concentration as a function of total alkali content

OH ion quantity per gramme cement as a function of total alkali content

Fig 4.18



Appendix 5

TABLE 5.1 PFA REPLACEMENTS AT 28 days

OPC/PFA	Cement Total K/Na mmol/g	IONIC CONCENTRATION mmols/L				WE g/g	QTY OF IONS IN SOLN mmol/g			IONS IN SOLN CEMENT ONLY (%)		EQ. OH DILUTION FACTOR	
		OH	pH	K	Na		OH	K	Na	K	Na	Conc	Qty
CEMENT A	26/39	203	13,31	94	94	0,281	57	26	26	100	67		
90 10		185	13,27	123	89	0,303	56	37	27	142	69	9	2
80 20		217	13,34	198	101	0,335	73	66	34	254	87	+7	28
70 30		209	13,32	175	90	0,343	72	60	31	231	79	+3	26
60 40		212	13,33	173	75	0,360	77	62	27	238	69	+4	35
CEMENT B	179/39	626	13,80	457	134	0,292	183	123	39	74	100		
90 10		562	13,75	473	96	0,307	173	145	29	81	74	10	
80 20		524	13,72	447	99	0,318	167	142	31	79	79	16	9
70 30		459	13,66	394	94	0,326	150	128	31	72	79	27	18
60 40		414	13,62	350	102	0,335	139	118	34	65	87	34	24
CEMENT C	221/58	730	13,86	525	178	0,301	220	158	54	71	93		
90 10		660	13,82	504	110	0,328	217	165	36	75	62	10	1
80 20		629	13,80	465	112	0,325	205	151	36	68	62	14	7
70 30		561	13,75	447	102	0,341	191	152	35	69	60	23	13
60 40		524	13,72	414	96	0,366	192	152	35	69	60	28	13
CEMENT D	204/197	806	13,91	479	303	0,285	229	137	86	67	44		
90 10		758	13,88	540	207	0,319	242	172	66	84	34	6	+6
80 20		707	13,85	496	227	0,332	235	165	75	81	38	12	+2
70 30		707	13,85	496	221	0,333	236	165	74	81	38	12	+3
60 40		645	13,81	476	187	0,347	224	165	65	81	33	20	2

TABLE 5,2 PFA REPLACEMENTS AT 168 DAYS

OPC/PFA	Total Cement K/Na mmol/g	IONIC CONCENTRATION mmol/l				We g/g	QTY OF IONS IN SOLN mmol/g			IONS IN SOLN (%)		EQ.OH.DILUTION FACTOR	
		OH	pH	K	Na		OH	K	Na	K	Na	Conc	Qty
CEMENT A	26/39	224	13,35	95	116	0,260	58	25	30	96	77		
90 10		251	13,40	116	93	0,288	72	48	27	+185	69	+12	+24
80 20		267	13,43	169	89	0,269	72	45	24	+173	62	+20	+24
70 30		246	13,39	158	81	0,319	79	50	26	+192	67	+10	+35
60 40		254	13,41	167	84	0,317	81	53	27	+204	69	+13	+38
CEMENT B	179/39	661	13,82	472	156	0,251	166	118	39	66	100		
90 10		555	13,74	444	111	0,285	158	127	32	71	82	9	5
80 20		449	13,65	357	96	0,291	131	104	28	58	72	28	21
70 30		393	13,59	331	98	0,303	119	100	30	56	77	37	28
60 40		371	13,57	266	89	0,300	111	80	27	45	69	40	33
CEMENT C	221/58	771	13,89	521	169	0,264	204	138	45	62	78		
90 10		676	13,83	540	145	0,293	198	158	42	71	72	10	
80 20		575	13,76	444	118	0,299	172	133	35	60	60	24	16
70 30		503	13,70	393	113	0,322	162	127	36	57	62	33	20
60 40		453	13,66	362	103	0,327	148	118	34	53	59	40	27
CEMENT D	204/197	829	13,92	468	292	0,270	224	126	79	62	40		
90 10		772	13,89	540	222	0,295	228	162	65	79	33	7	+2
80 20		608	13,78	389	251	0,283	172	121	53	59	27	27	23
70 30		583	13,77	350	200	0,289	169	120	53	59	27	30	25
60 40		550	13,74	300	170	0,298	164	117	51	57	26	34	27

TABLE 5,3

PFA REPLACEMENTS AT 365 days

OPC/PFA	Total Cement K/Na mmol/g	IONIC CONCENTRATION mmols/L				WE g/g	QTY OF IONS IN SOLN mmol/g			IONS IN SOLN CEMENT ONLY (%)		EQ. OH DILUTION FACTOR	
		OH	pH	K	Na		OH	K	Na	K	Na	Conc	Qty
CEMENT A	26/39	227	13,39	92	129	0,257	58	24	33	92	85		
90 10		279	13,48	176	95	0,286	80	50	27	+192	69	+21	+34
80 20		284	13,45	182	93	0,265	75	48	25	+185	64	+15	+18
70 30		274	13,43	162	85	0,312	86	51	27	+196	69	+11	+35
60 40		256	13,40	158	73	0,330	85	52	24	+200	62	+13	+33
CEMENT B	179/39	661	13,82	474	161	0,249	165	118	40	66	100		
90 10		547	13,74	363	156	0,255	140	93	40	52	100	17	15
80 20		451	13,66	295	116	0,262	118	77	30	43	77	32	28
70 30		412	13,62	286	90	0,287	118	82	26	46	67	38	28
60 40		386	13,59	256	86	0,290	112	74	25	41	64	42	32
CEMENT C	221/58	753	13,88	505	177	0,262	197	132	46	60	79		
90 10		687	13,84	489	195	0,277	191	135	54	61	93	9	3
80 20		529	13,72	337	164	0,298	158	100	49	45	84	30	20
70 30		480	13,68	296	158	0,302	145	89	48	40	83	36	26
60 40		438	13,64	263	146	0,311	136	82	45	37	78	42	31
CEMENT D	204/197	810	13,91	465	315	0,257	208	120	81	59	41		
90 10		756	13,88	408	303	0,275	208	112	83	55	42	7	0
80 20		575	13,76	292	265	0,279	161	81	74	40	38	29	23
70 30		554	13,74	281	213	0,286	158	80	61	39	31	32	24
60 40		520	13,72	267	199	0,295	154	79	59	39	30	36	26

TABLE 5.4 OH ions removed by Pfa

Cement	(OH ions removed between 28 and 365 days) OH ions removed per g Pfa			
	10%	20%	30%	40%
A (1)	(+25)	(+3)	(+15)	(+9)
	250	15	50	23
B (18)	(15)	(31)	(14)	(9)
	150	155	47	23
C (23)	(3)	(24)	(23)	(33)
	30	120	77	83
D (21)	(13)	(53)	(57)	(49)
	130	265	190	123

TABLE 5.5 K ions removed by Pfa

Cement	(K ions removed between 28 and 365 days) K ions removed per g Pfa			
	10%	20%	30%	40%
(2)	(+15)	(16)	(7)	(8)
	+150	80	23	20
(15)	(37)	(50)	(31)	(29)
	370	250	103	73
(26)	(4)	(25)	(37)	(44)
	40	125	123	110
(17)	(43)	(67)	(68)	(67)
	430	335	227	173

TABLE 5.6 Na ions removed by Pfa

Cement	(Na ions removed between 28 and 365 days) Na ions removed per g Pfa			
	10%	20%	30%	40%
(+7)	(+7)	(16)	(11)	(10)
	+70	80	37	25
(0)	(+11)	(1)	(5)	(9)
	+110	5	17	23
(8)	(+18)	(+21)	(+21)	(+18)
	180	+105	+70	+45
(5)	(+25)	(+24)	(8)	(1)
	+250	+120	27	2.5

mmols/g

TABLE 5.4 OH ions removed by Pfa

Cement	(OH ions removed between 28 and 365 days) OH ions removed per g Pfa			
	10%	20%	30%	40%
A (1)	(+25) 250	(+3) 15	(+15) 50	(+9) 23
B (18)	(15) 150	(31) 155	(14) 47	(9) 23
C (23)	(3) 30	(24) 120	(23) 77	(33) 83
D (21)	(13) 130	(53) 265	(57) 190	(49) 123

TABLE 5.5 K ions removed by Pfa

Cement	(K ions removed between 28 and 365 days) K ions removed per g Pfa			
	10%	20%	30%	40%
(2)	(+15) +150	(16) 80	(7) 23	(8) 20
(15)	(37) 370	(50) 250	(31) 103	(29) 73
(26)	(4) 40	(25) 125	(37) 123	(44) 110
(17)	(43) 430	(67) 335	(68) 227	(67) 173

TABLE 5.6 Na ions removed by Pfa

Cement	(Na ions removed between 28 and 365 days) Na ions removed per g Pfa			
	10%	20%	30%	40%
(+7)	(+7) +70	(16) 80	(11) 37	(10) 25
(0)	(+11) +110	(1) 5	(5) 17	(9) 23
(8)	(+18) 180	(+21) +105	(+21) +70	(+18) +45
(5)	(+25) +250	(+24) +120	(8) 27	(1) 2.5

mmols/g

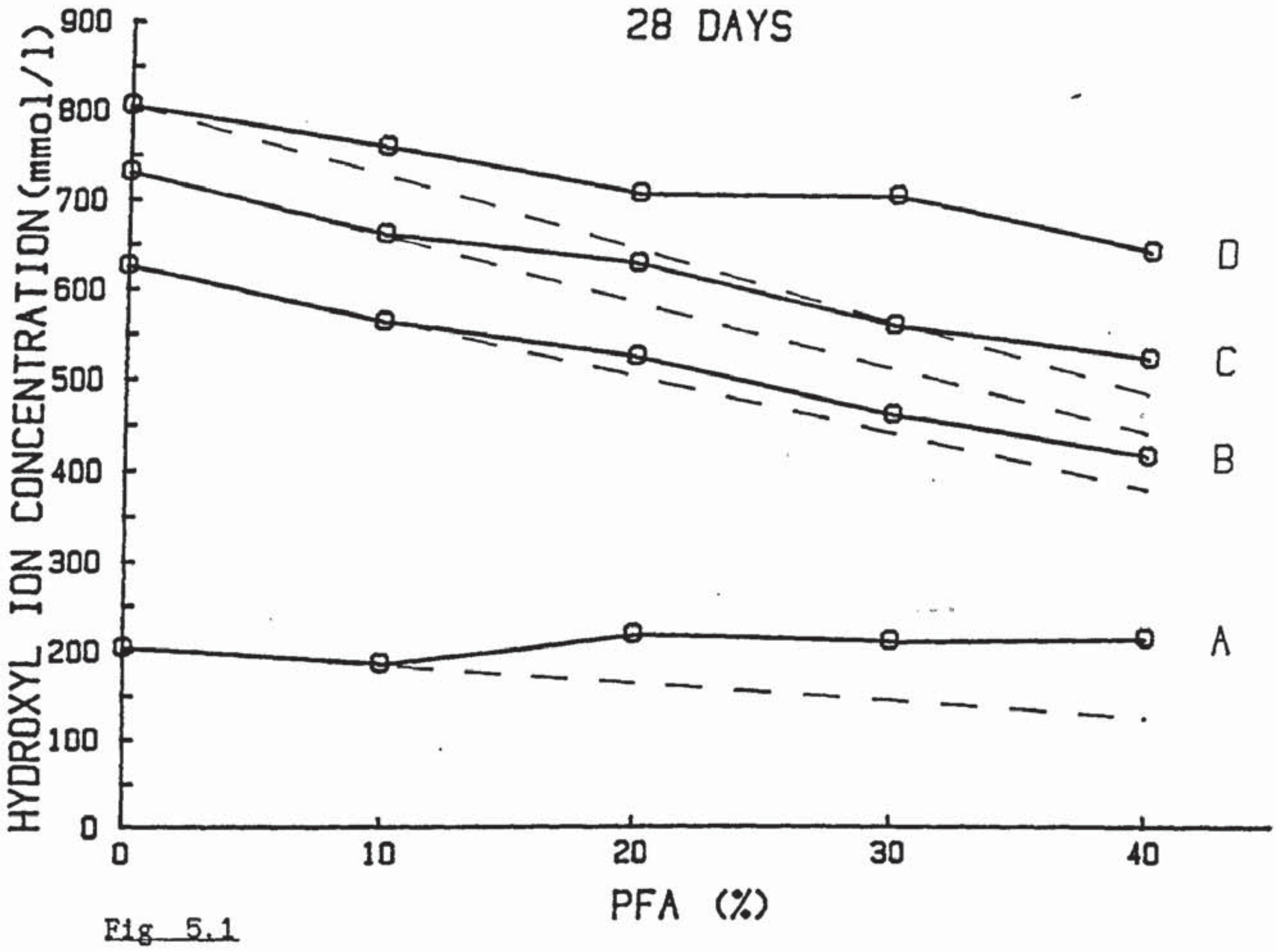
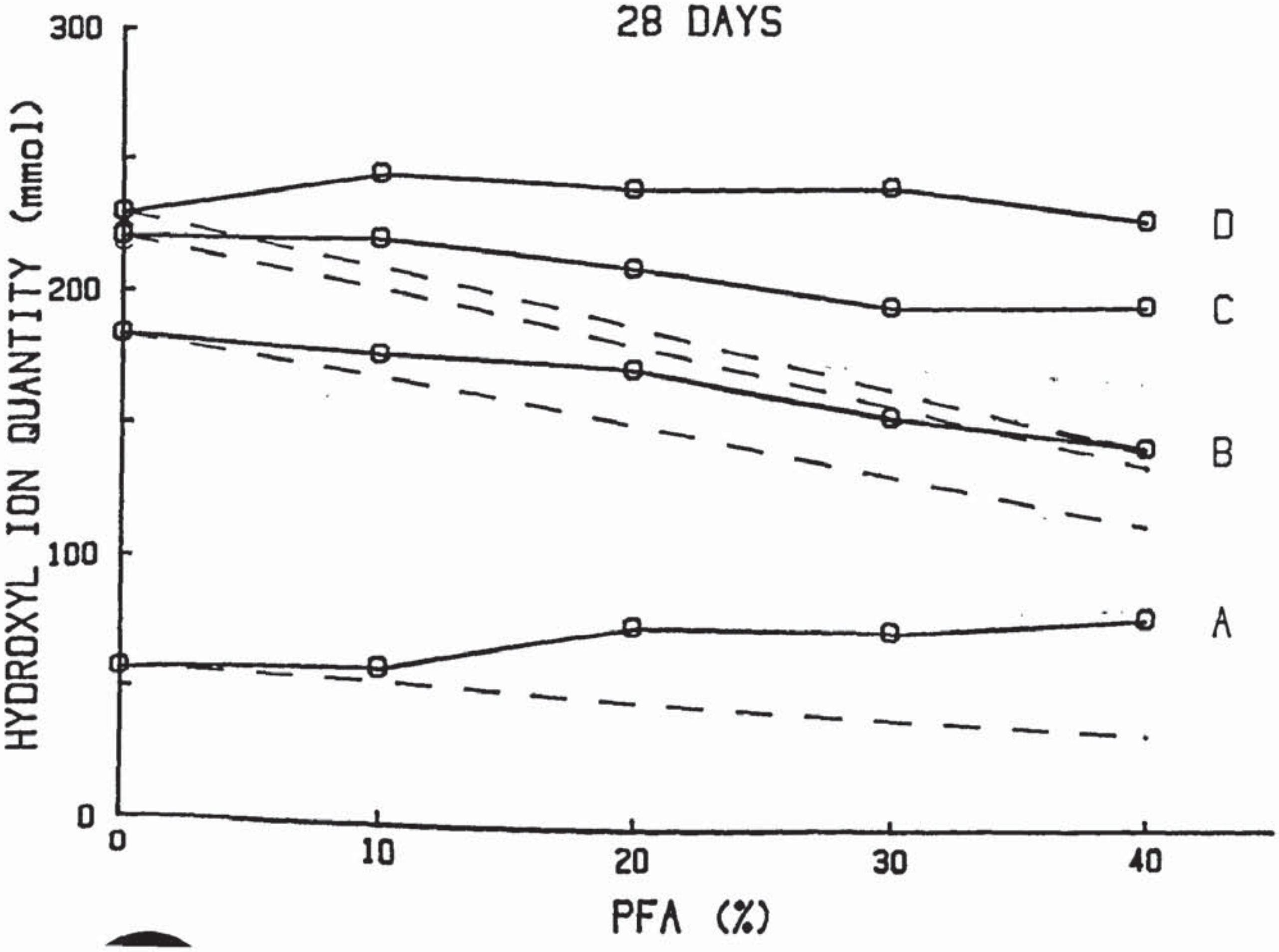


Fig 5.1

Hydroxyl ions in solution of cements substituted by pfa

Fig 5.2



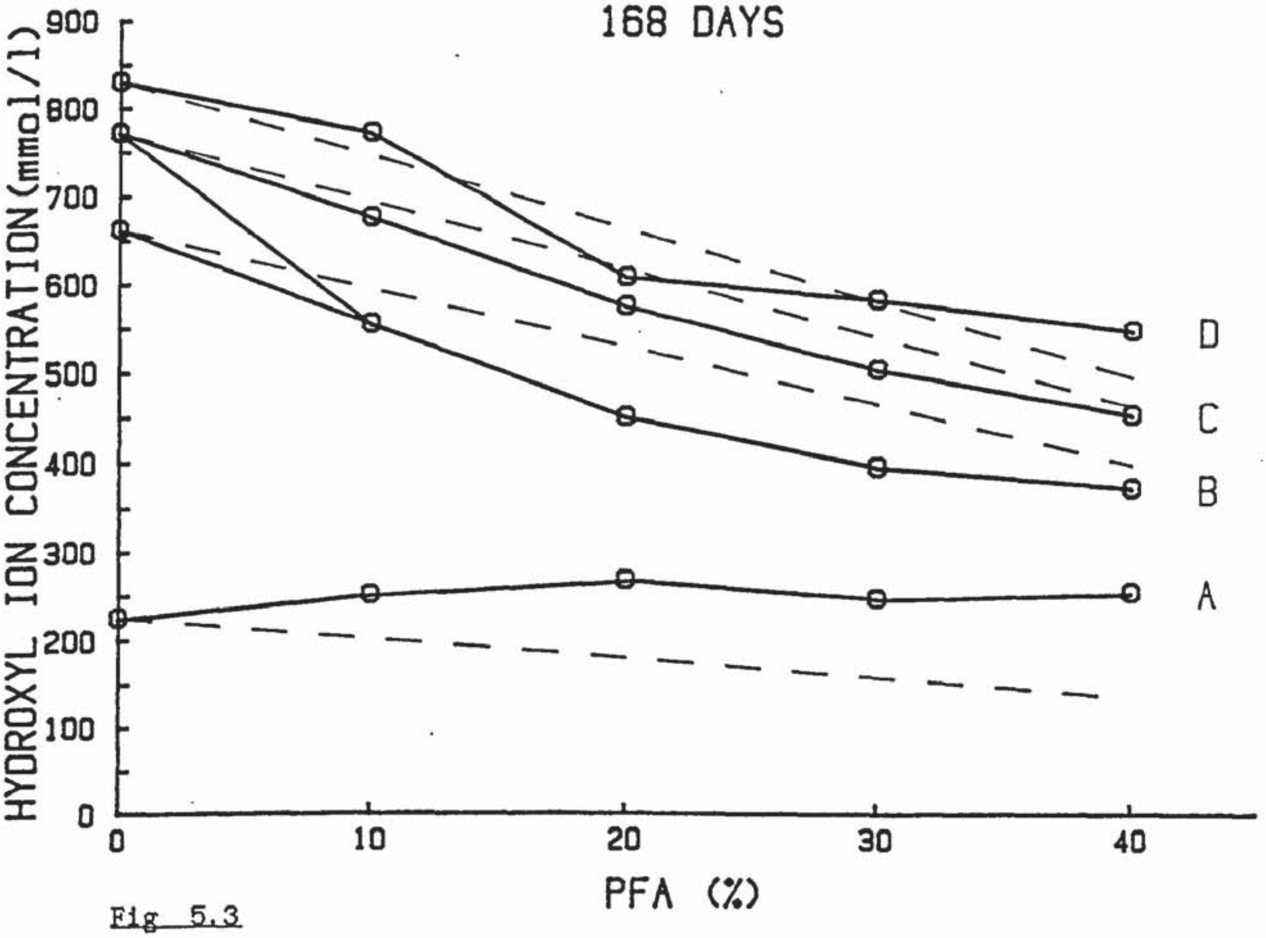
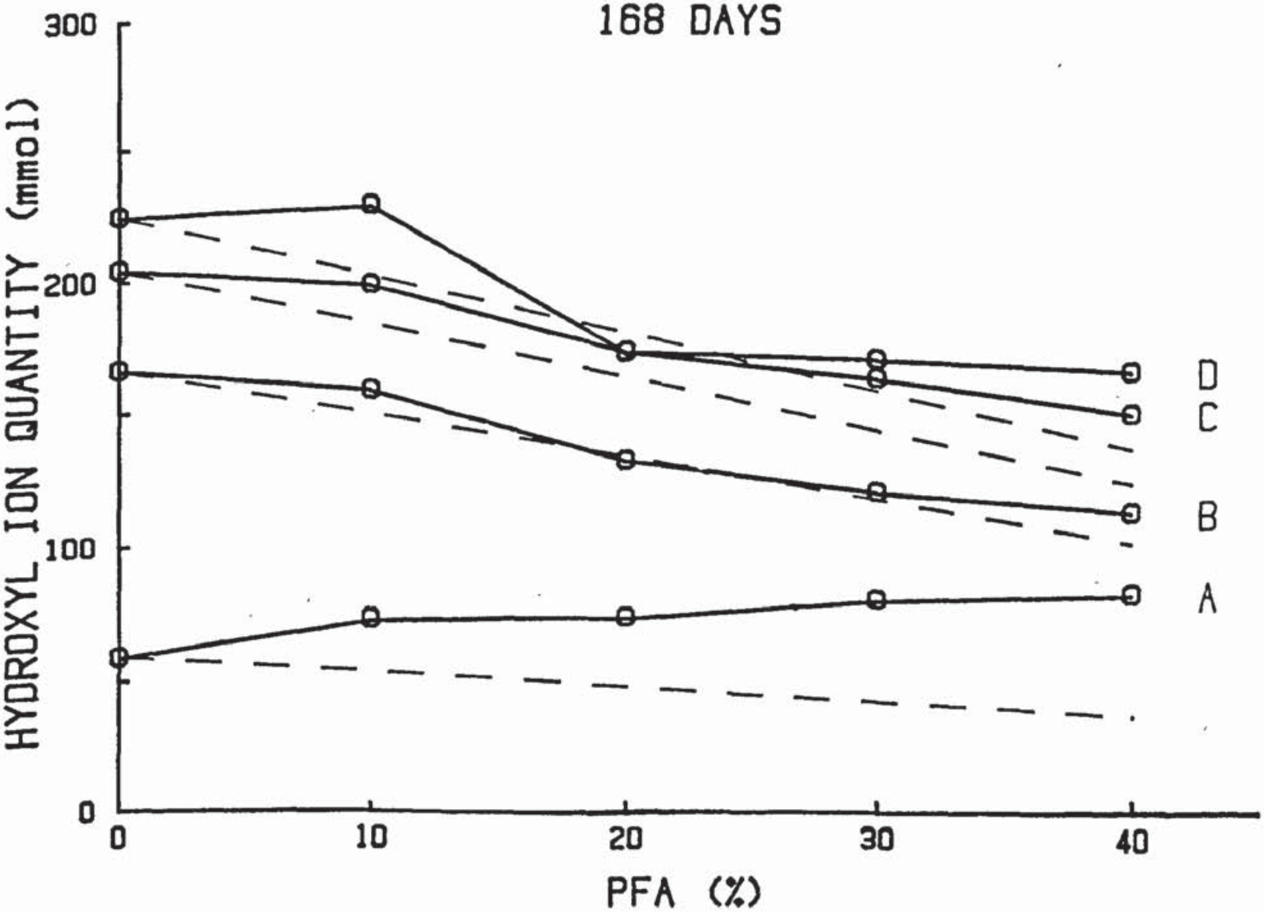


Fig 5.3

Hydroxyl ions in solution of cements substituted by pfa

Fig 5.4



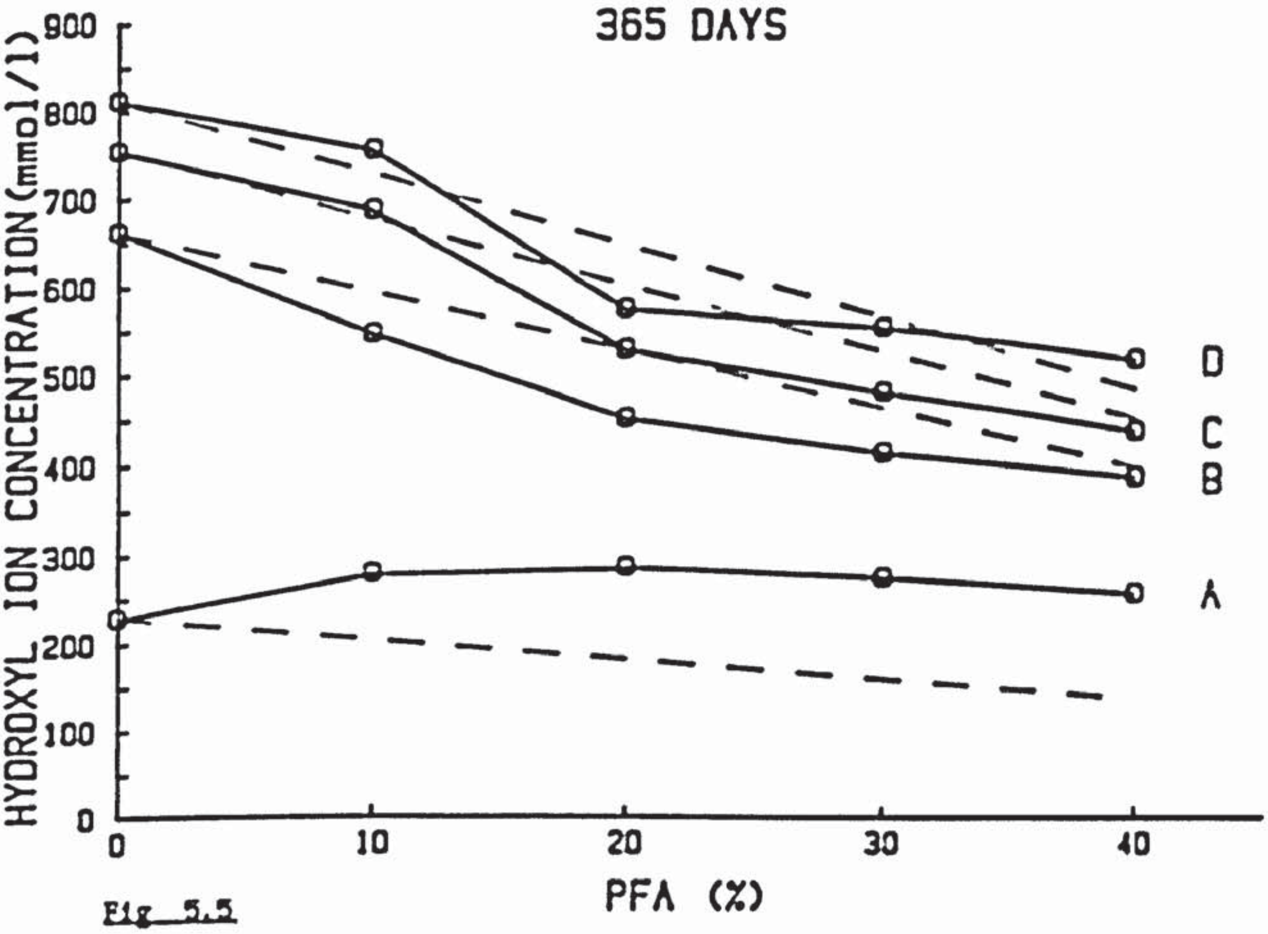
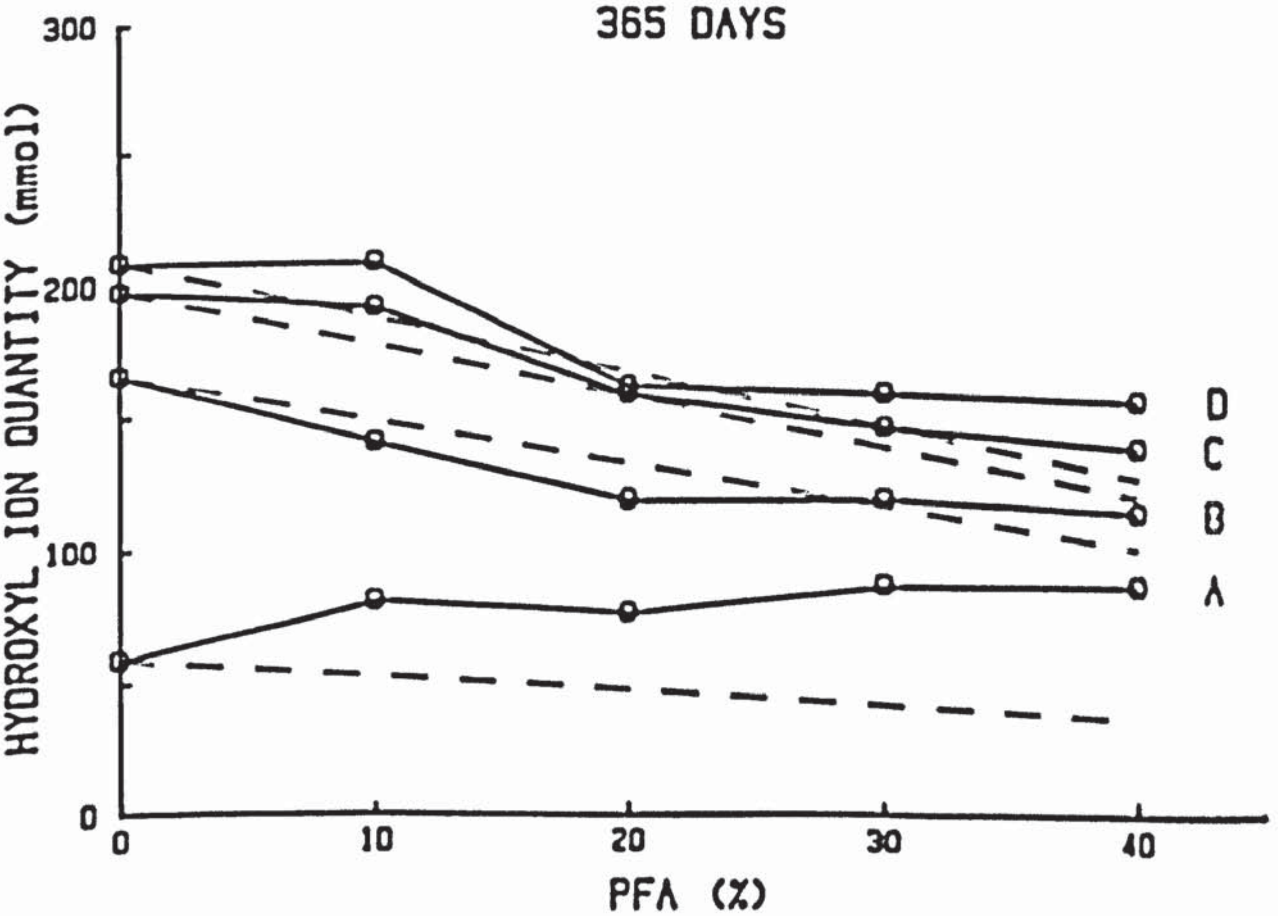


Fig 5.5

Hydroxyl ions in solution of cements substituted by pfa

Fig 5.6



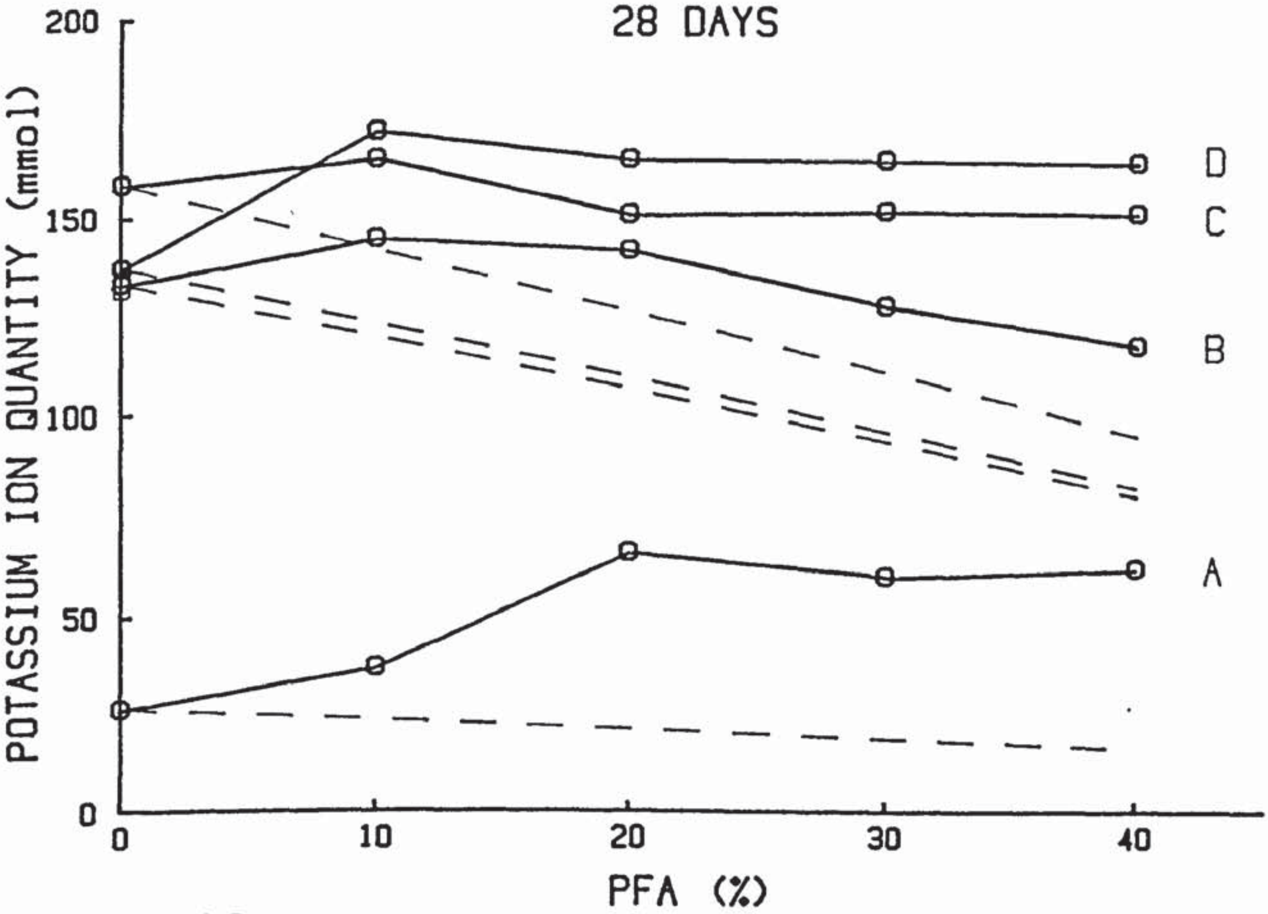
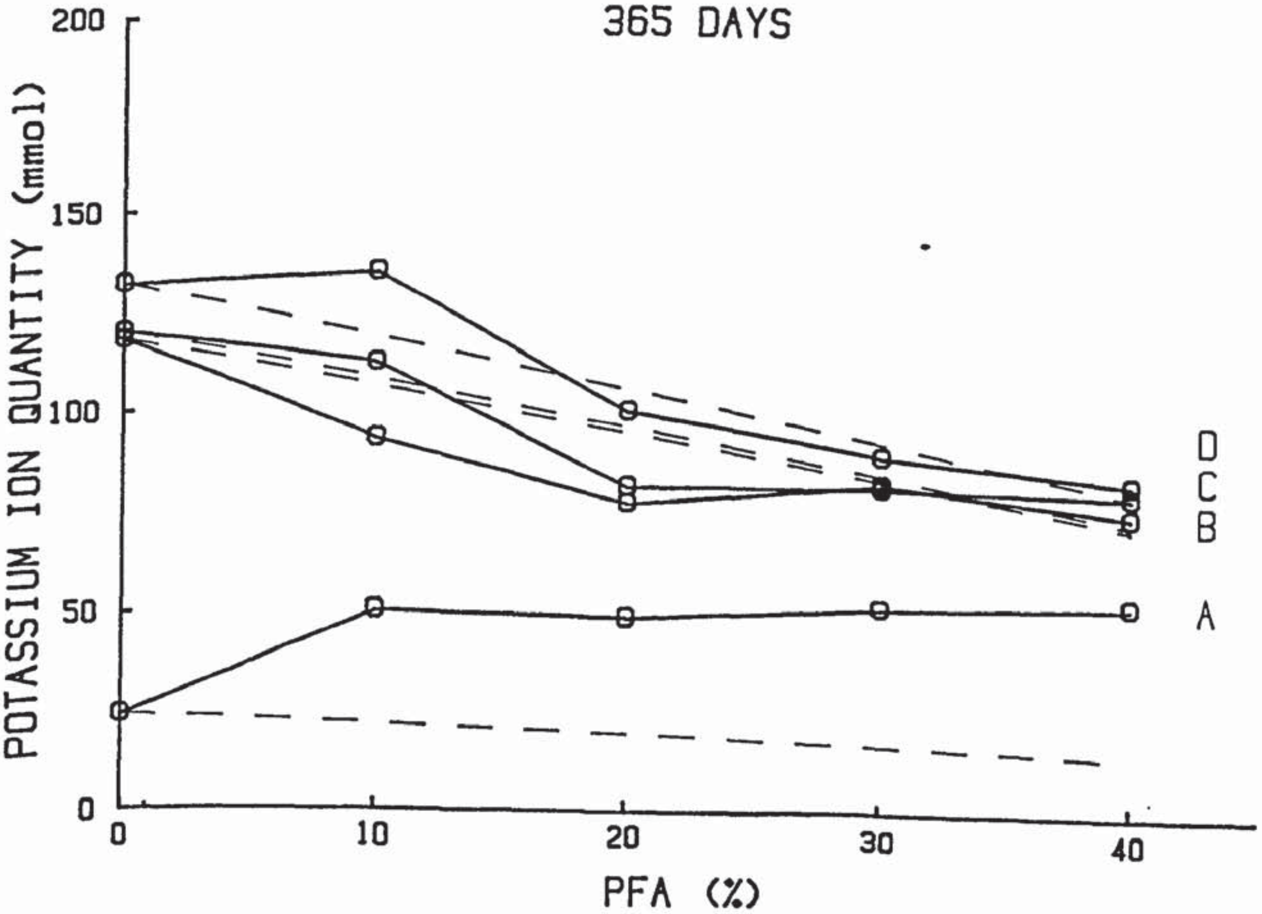


Fig 5.7

Potassium ions in solution of cements substituted by pfa

Fig 5.8



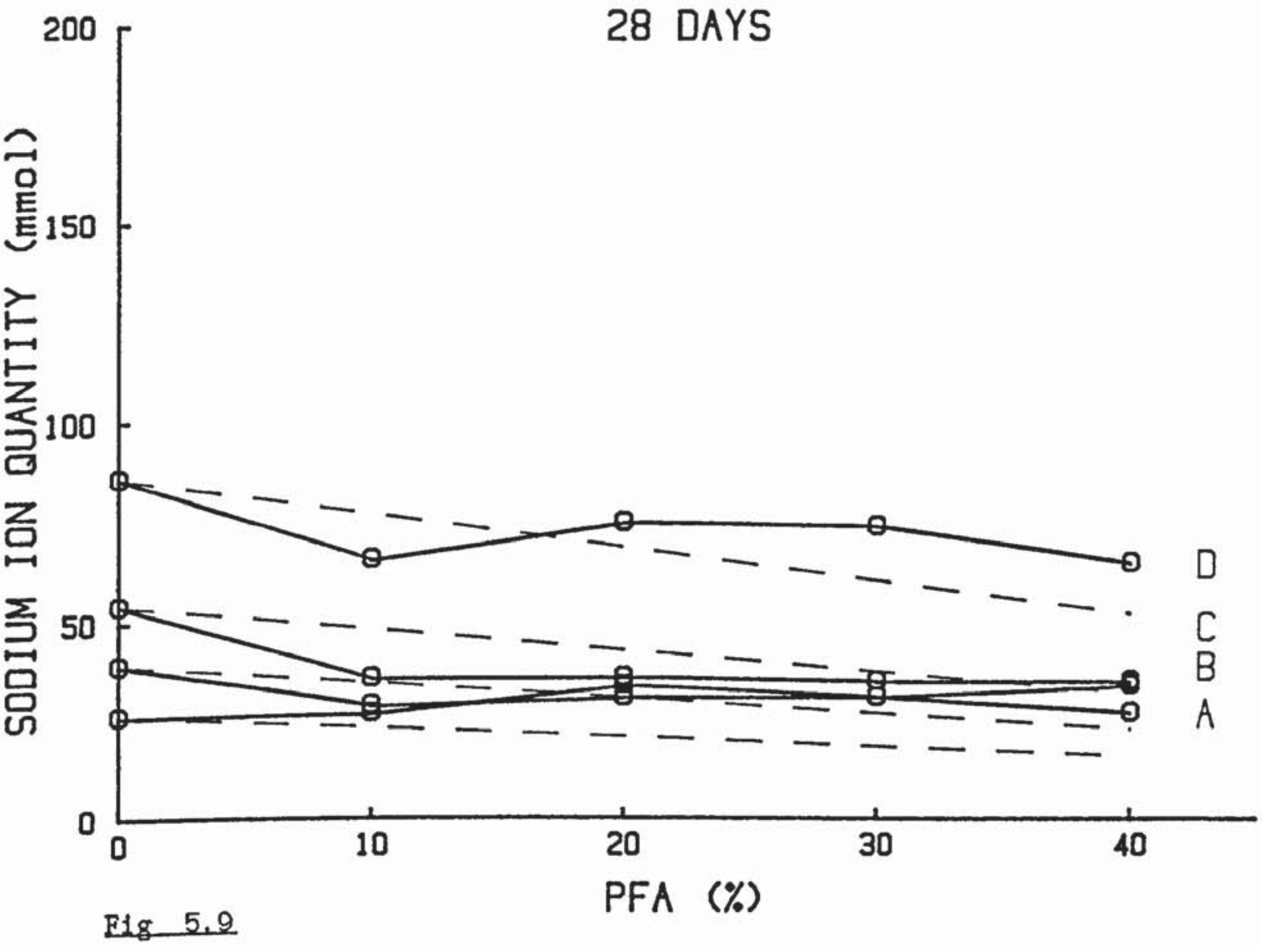


Fig 5.9

Sodium ions in solution of cements substituted by pfa

Fig 5.10

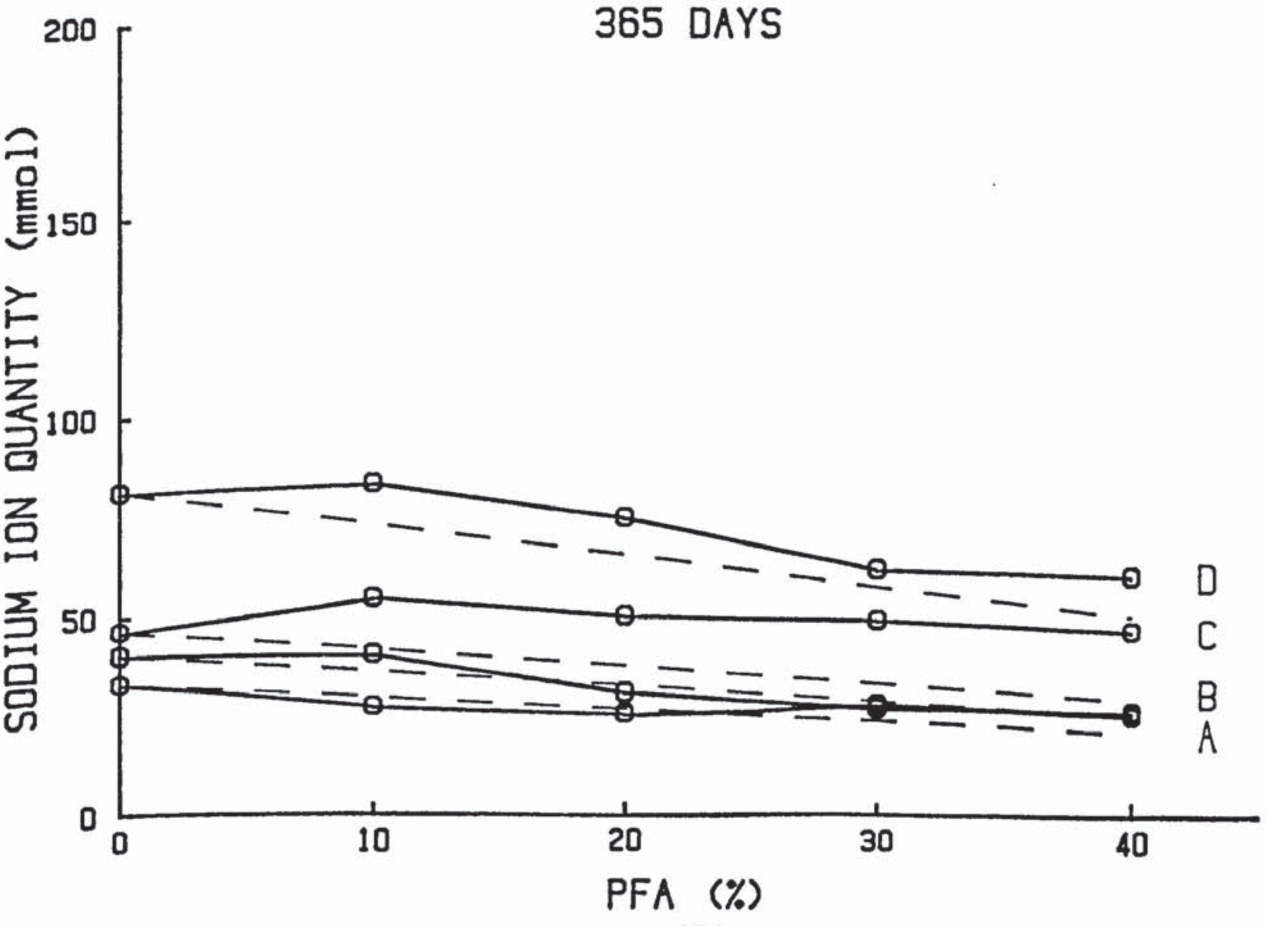


TABLE 5,7 SLAG REPLACEMENTS AT 28 days

OPC/SLAG	Total Cement K/Na	IONIC CONCENTRATION mmols/l				WE g/g	QTY OF IONS IN SOLN mmol/g			IONS IN SOLN CEMENT ONLY (%)		EQ, OH DILUTION FACTOR	
	mmol/g	OH	pH	K	Na		OH	K	Na	K	Na	Conc	Qty
CEMENT A	26/39	203	13,31	94	93	0,281	57	26	26	100	67		
60 40		216	13,34	80	121	0,333	72	27	40	104	103	+6	+26
40 60		172	13,24	58	98	0,340	58	20	33	77	85	15	+2
20 80		128	13,12	43	70	0,356	46	15	25	58	64	37	19
CEMENT B	179/39	626	13,80	457	141	0,292	183	133	41	74	10		
60 40		430	13,63	251	147	0,304	126	73	43	41	110	31	31
40 60		296	13,47	150	123	0,318	94	48	39	27	100	53	49
20 80		188	13,28	60	80	0,345	65	21	28	12	72	70	64
CEMENT C	221/58	730	13,86	525	178	0,301	220	158	54	71	93		
60 40		473	13,68	295	179	0,301	142	89	54	40	93	35	35
40 60		309	13,49	169	148	0,336	104	57	50	26	86	58	53
20 80		197	13,29	98	83	0,356	70	35	30	16	52	73	68
CEMENT D	204/197	805	13,91	479	303	0,285	229	137	86	67	44		
60 40		533	13,73	290	231	0,293	156	85	68	76	35	34	32
40 60		331	13,52	160	157	0,322	107	52	51	25	26	59	53
20 80		196	13,29	84	108	0,352	69	30	38	15	19	76	70

TABLE 5.8

SLAG REPLACEMENTS AT 168 days

OPC/SLAG	Total Cement K/Na	IONIC CONCENTRATION mmols/L				WE g/g	QTY OF IONS IN SOLN mmol/g			IONS IN SOLN CEMENT ONLY (%)		EQ. OH DILUTION FACTOR	
	mmol/g	OH	pH	K	Na		OH	K	Na	K	Na	Conc	Qty
CEMENT A	26/39	224	13,35	95	116	0,260	58	25	30	96	77		
60 40		236	13,37	90	132	0,296	70	27	39	104	100	+5	+21
40 60		181	13,25	64	109	0,326	59	21	36	81	92	19	+2
20 80		137	13,14	40	87	0,346	47	14	30	54	36	39	19
CEMENT B	179/39	661	13,82	472	156	0,251	166	118	39	66	100		
60 40		429	13,63	240	157	0,278	119	67	44	37	113	35	28
40 60		289	13,46	150	129	0,291	84	44	38	24	97	56	49
20 80		188	13,27	78	90	0,326	61	25	29	14	74	72	63
CEMENT C	221/58	771	13,89	521	169	0,264	204	138	45	62	78		
60 40		459	13,66	286	173	0,282	129	81	49	37	84	40	37
40 60		300	13,48	150	146	0,299	90	45	44	20	76	61	56
20 80		198	13,30	95	82	0,319	63	30	26	14	45	74	69
CEMENT D	204/197	829	13,92	468	292	0,270	224	126	79	62	40		
60 40		512	13,71	269	210	0,275	141	74	58	36	29	38	37
40 60		297	13,47	132	139	0,301	89	40	42	20	21	64	60
20 80		182	13,26	76	94	0,322	59	26	30	12	15	78	74

TABLE 5,9

SLAG REPLACEMENTS AT 365 days

OPC/SLAG	Total Cement K/Na	IONIC CONCENTRATION mmols/L				WE g/g	QTY OF IONS IN SOLN mmol/g			IONS IN SOLN CEMENT ONLY (%)		EQ. OH DILUTION FACTOR	
	mmol/g	OH	pH	K	Na		OH	K	Na	K	Na	Conc	Qty
CEMENT A	26/39	247	13,39	92	129	0,257	64	24	33	92	85		
60 40		259	13,41	94	153	0,287	74	27	44	104	113	+5	+16
40 60		193	13,29	66	118	0,322	62	22	38	85	97	22	3
20 80		132	13,12	40	91	0,343	45	14	31	54	79	47	30
CEMENT B	179/39	661	13,82	474	140	0,249	165	118	35	66	90		
60 40		418	13,62	231	148	0,275	115	64	41	36	105	37	30
40 60		288	13,46	143	139	0,287	83	41	40	23	103	56	50
20 80		178	13,25	76	97	0,310	55	24	31	13	79	73	67
CEMENT C	221/58	753	13,88	505	177	0,262	197	132	46	60	79		
60 40		480	13,68	280	176	0,278	133	78	49	35	84	36	32
40 60		302	13,48	144	142	0,285	86	45	40	19	69	60	56
20 80		175	13,26	90	80	0,315	55	28	30	13	43	77	72
CEMENT D	204/197	810	13,91	465	315	0,257	208	120	81	59	41		
60 40		502	13,70	247	254	0,262	132	65	67	32	34	38	37
40 60		264	13,42	128	131	0,289	76	37	44	18	19	67	63
20 80		162	13,21	74	92	0,310	50	23	30	11	15	80	76

TABLE 5.10

OH IONS REMOVED BY SLAG

CEMENT (*)	OH ions removed between 28 and 365 days by slag		
	40%	60%	80%
A (+7)	5	3	8
B (18)	+7	+7	+8
C (23)	+14	+5	+8
D (21)	3	10	+3

TABLE 5.11

K IONS REMOVED BY SLAG

CEMENT (*)	K ions removed between 28 and 365 days by slag		
	40%	60%	80%
A (2)	+2	4	1
B (15)	6	8	+18
C (26)	+15	+10	+19
D (17)	3	+27	+10

TABLE 5.12

Na IONS REMOVED BY SLAG

CEMENT (*)	Na ions removed between 28 and 365 days by slag		
	40%	60%	80%
A (+7)	3	2	1
B (6)	+4	+7	+9
C (8)	3	2	+3
D (5)	+4	+8	4

(*) Ions removed by cement

mmols

TABLE 5,13 PROPN,OF IONS IN SOLUTION

CEMENT Propn of slag		K IONS per g blend	PROPN OF K IONS IN SOLN % 28 days	168 days	365 days
	0	26	100	100	96
	40	16	169	169	169
A	60	10	200	210	220
	80	5	300	280	280
	0	179	74	66	66
	40	107	68	63	60
B	60	72	67	61	57
	80	36	58	69	67
	0	221	71	62	60
	40	133	67	61	59
C	60	88	65	51	47
	80	44	80	68	64
	0	204	67	62	59
	40	122	79	61	53
D	60	82	61	49	45
	80	41	73	58	56

TABLE5,14 PROPN,OF Na IONS IN SOLUTION

Na IONS from cement per g blend	PROPN OF Na IONS IN SOLN, % 28 days	168 days	365 days
39	67	77	85
23	174	169	191
16	206	225	238
8	313	375	388
39	100	100	90
23	187	191	178
16	244	238	250
8	350	363	387
59	93	78	79
35	154	140	140
23	217	191	174
12	250	217	208
197	44	40	41
118	58	49	57
79	65	53	48
39	97	77	74

nmols

TABLE 5,15 ESTIMATE OF K IONS CONTRIBUTED BY SLAG

CEMENT (slag propn) %	K ions from cement per g	Contribution by slag. 28 days	168 days	365 days
0	26	(100%)	(96%)	(92%)
40	16	+11	+23	+12
A 60	10	+10	+26	+13
80	5	+10	+25	+9
0	179	(74%)	(66%)	(66%)
* 40	107	-6	-4	-7
B 60	72	-5	-3	-6
80	36	-6	-1	0
0	221	(71%)	(62%)	(60%)
40	133	-6	-2	-1
C 60	88	-6	-10	-12
80	44	-4	-3	-2
* 0	204	(67%)	(62%)	(59%)
40	122	+3	+28	-7
D 60	82	-3	-11	-11
* 80	41	+2	-1	-1

TABLE 5,16 ESTIMATE OF Na IONS CONTRIBUTED BY SLAG

Na ions from cement per g	Contribution by slag 28 days	168 days	365 days
39	(67%)	(77%)	(65%)
23	+25	+21	+25
16	+22	+24	+24
8	+20	+24	+24
39	(100%)	(100%)	(90%)
23	+20	+21	+21
16	+23	+22	+26
8	+20	+21	+24
58	(93%)	(78%)	(79%)
35	+21	+22	+21
23	+29	+26	+22
12	+19	+17	+15
197	(44%)	(40%)	(41%)
118	+16	+11	+18
79	+17	+10	+32
39	+21	+14	+13

mmols

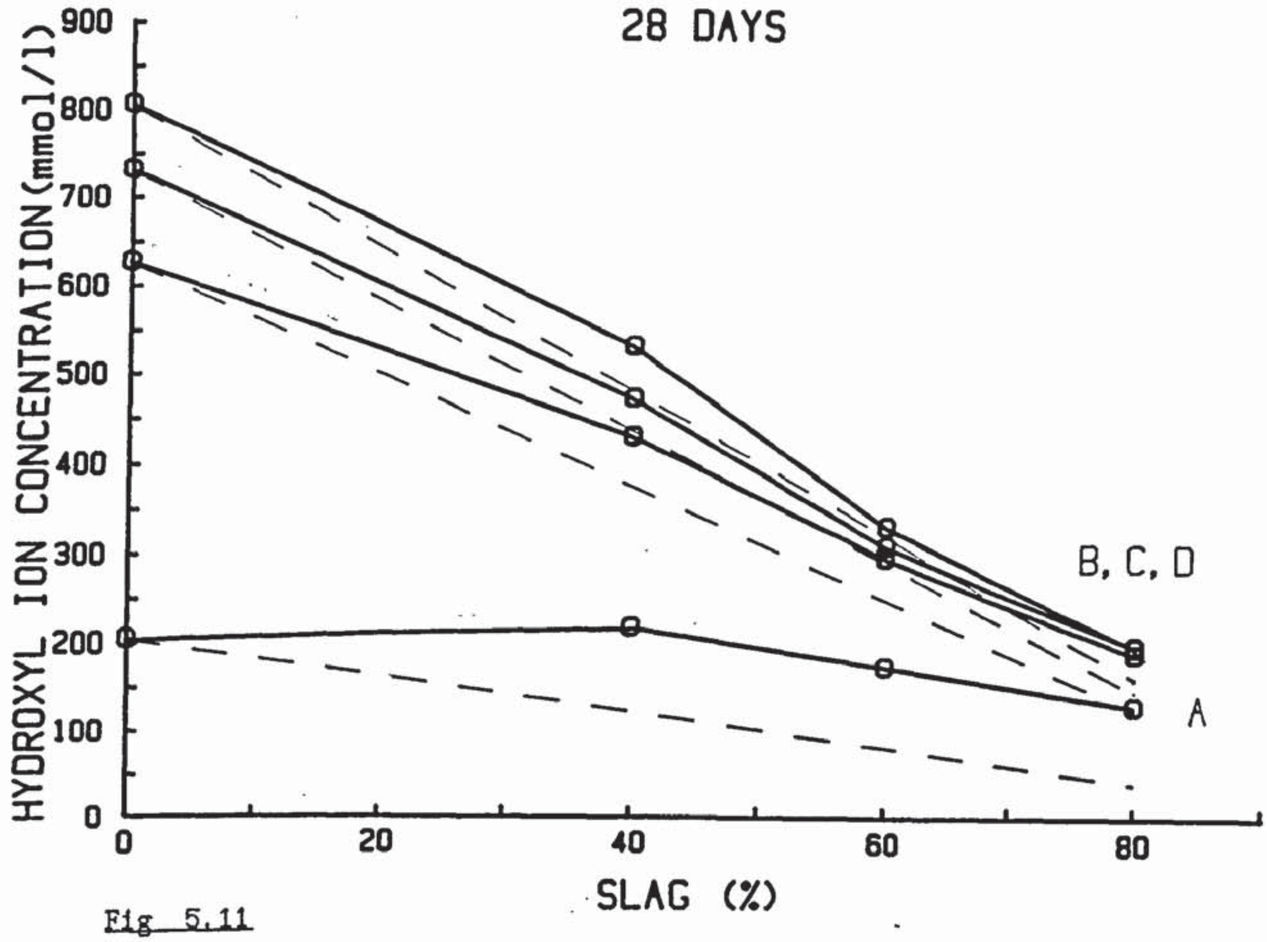
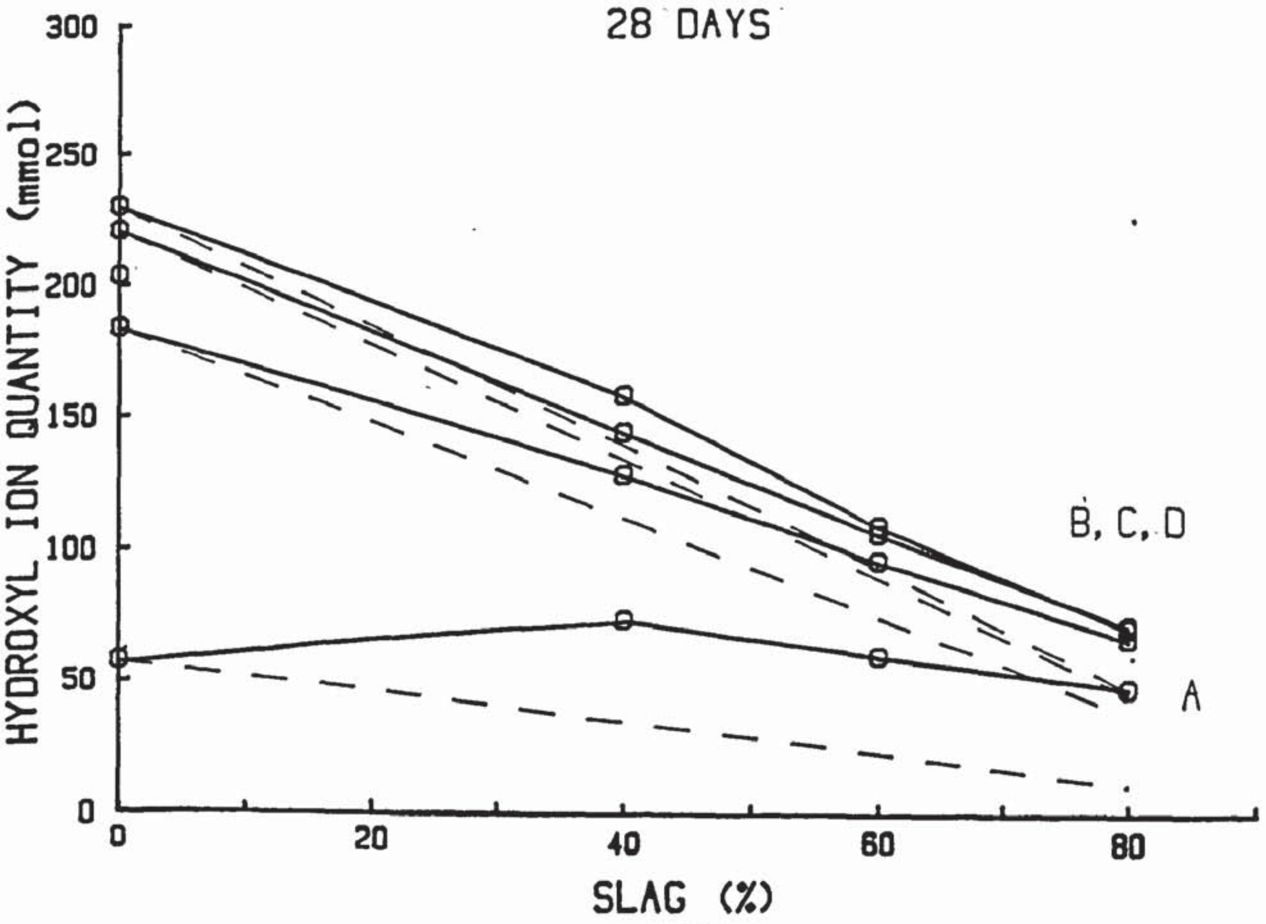


Fig 5.11

Hydroxyl ions in solution of cements substituted by gbfs

Fig 5.12



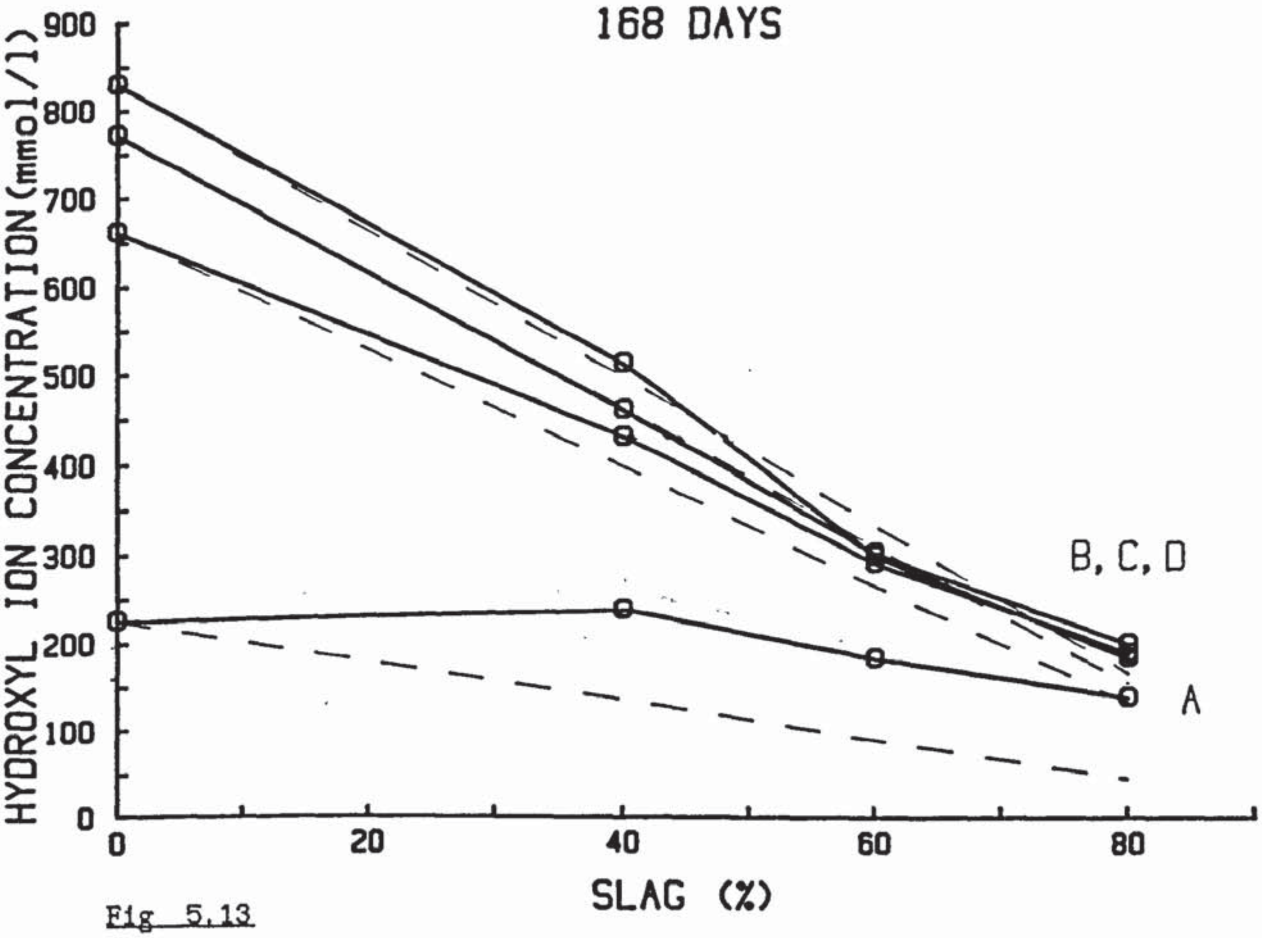
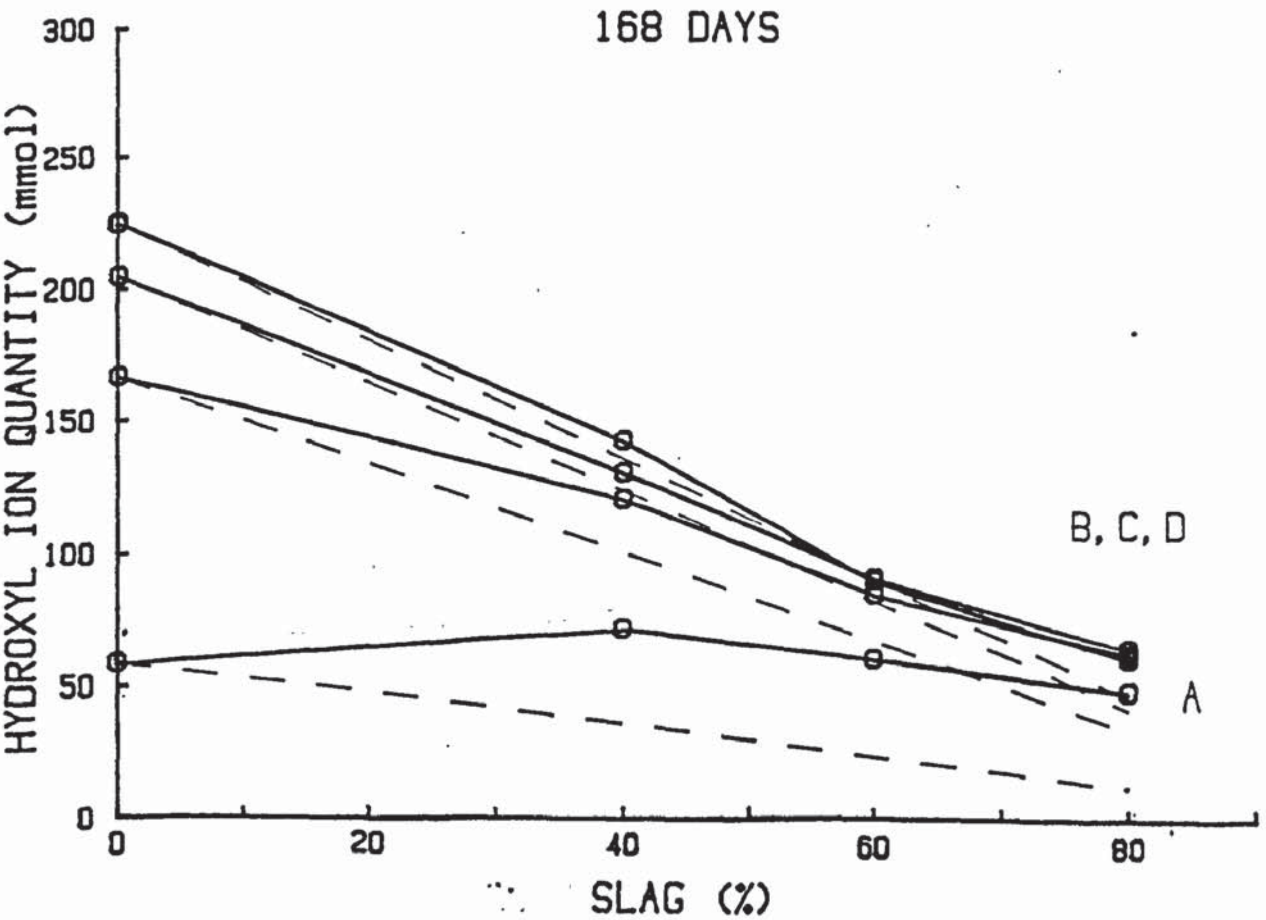


Fig 5.13

Hydroxyl ions in solution of cements substituted by gbfs

Fig 5.14



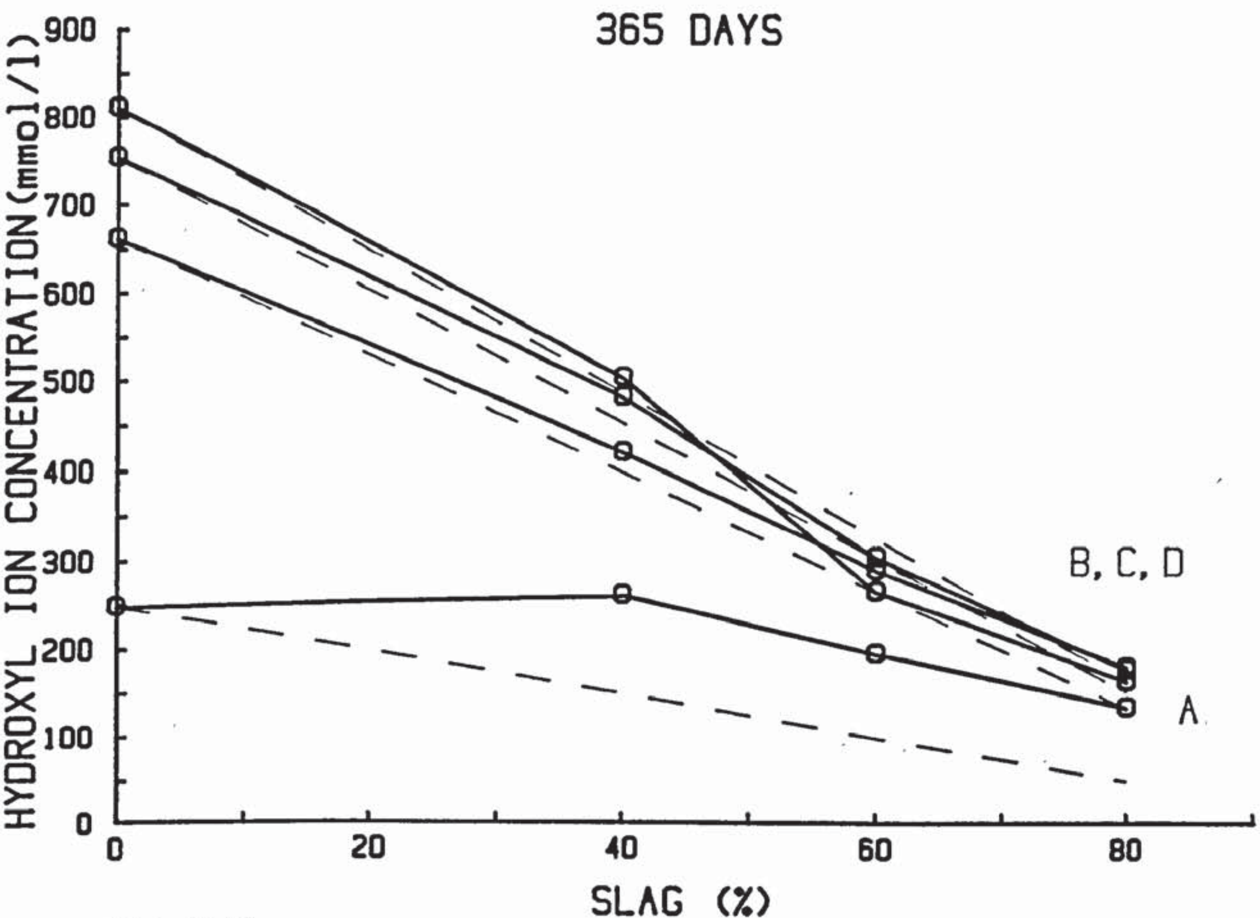
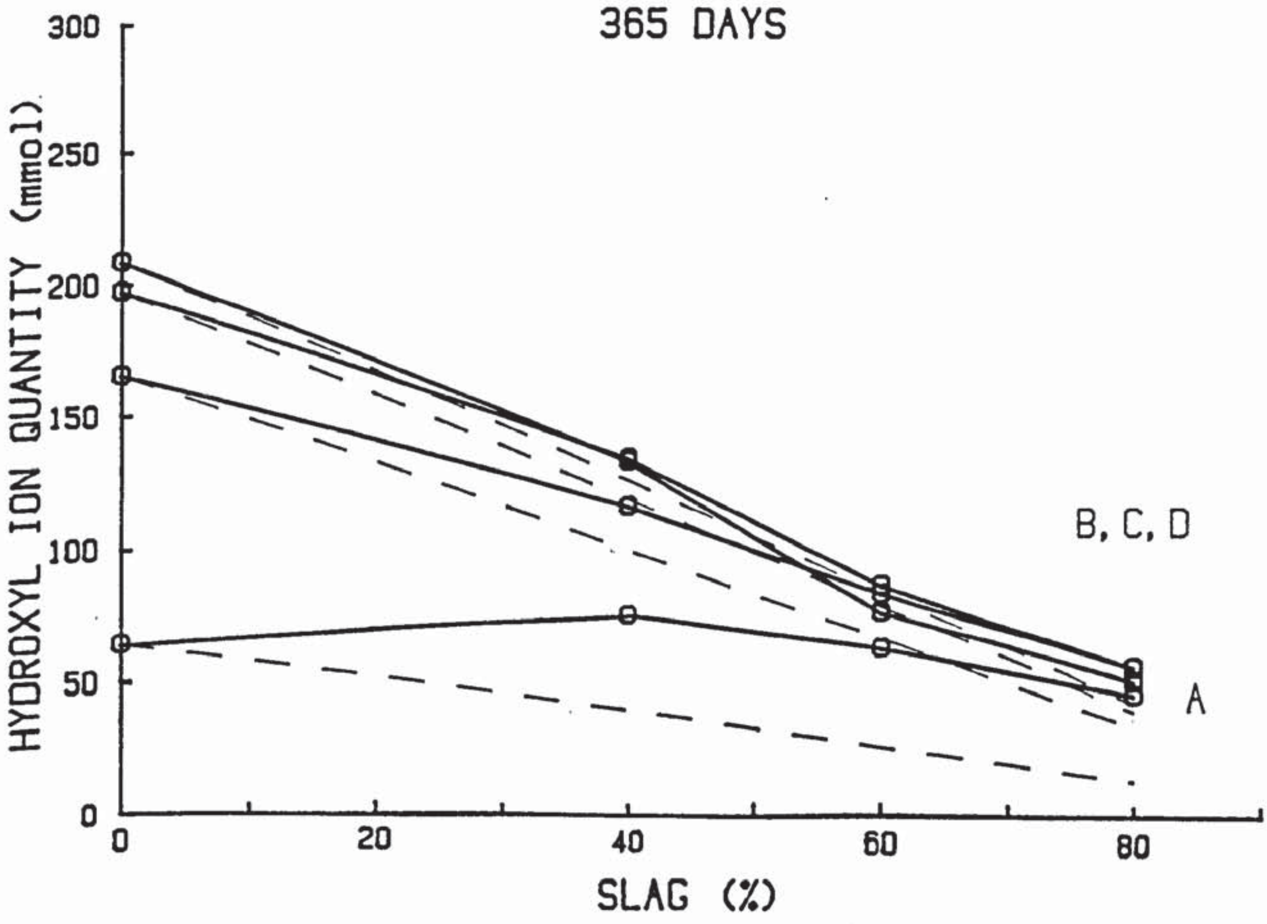


Fig 5.15

Hydroxyl ions in solution of cements substituted by gbfs

Fig 5.16



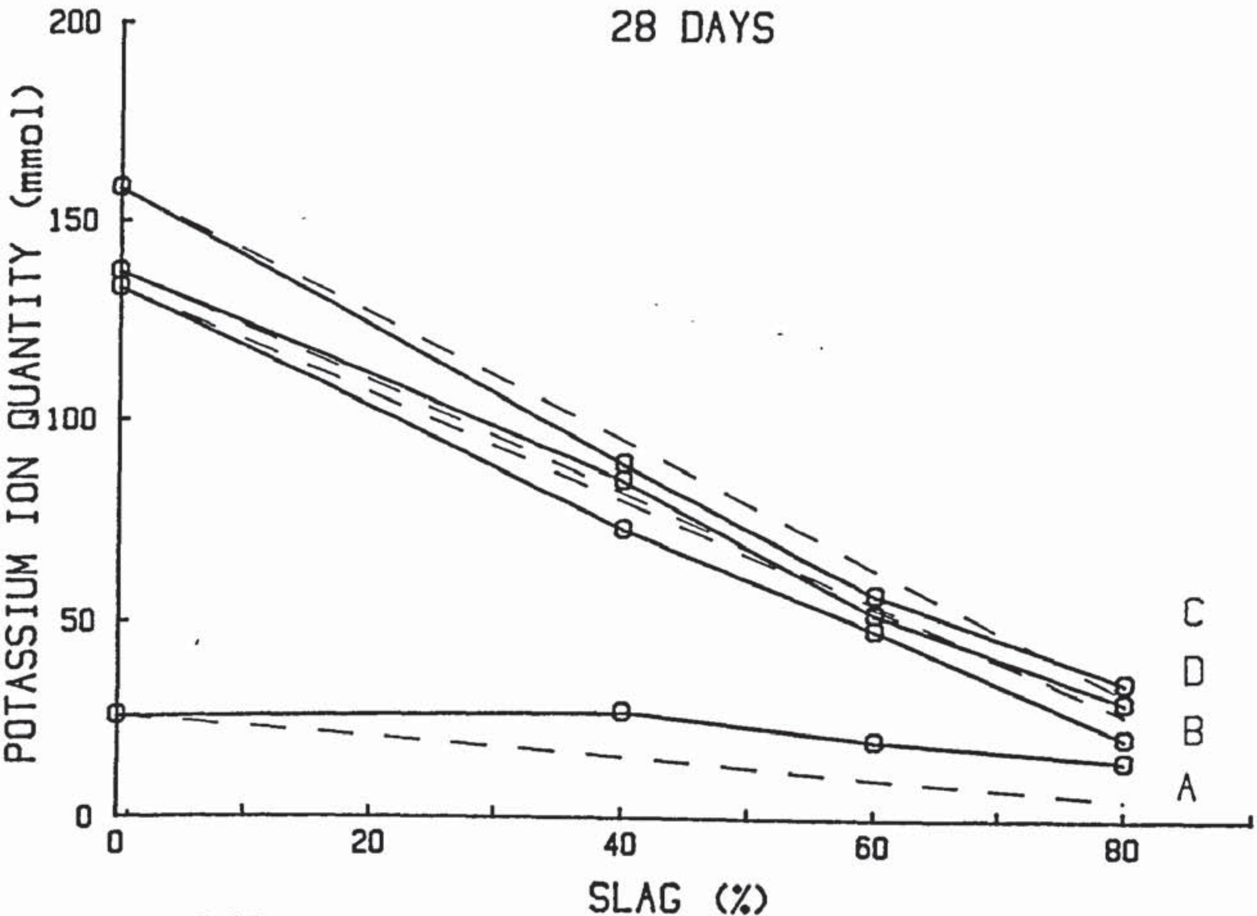
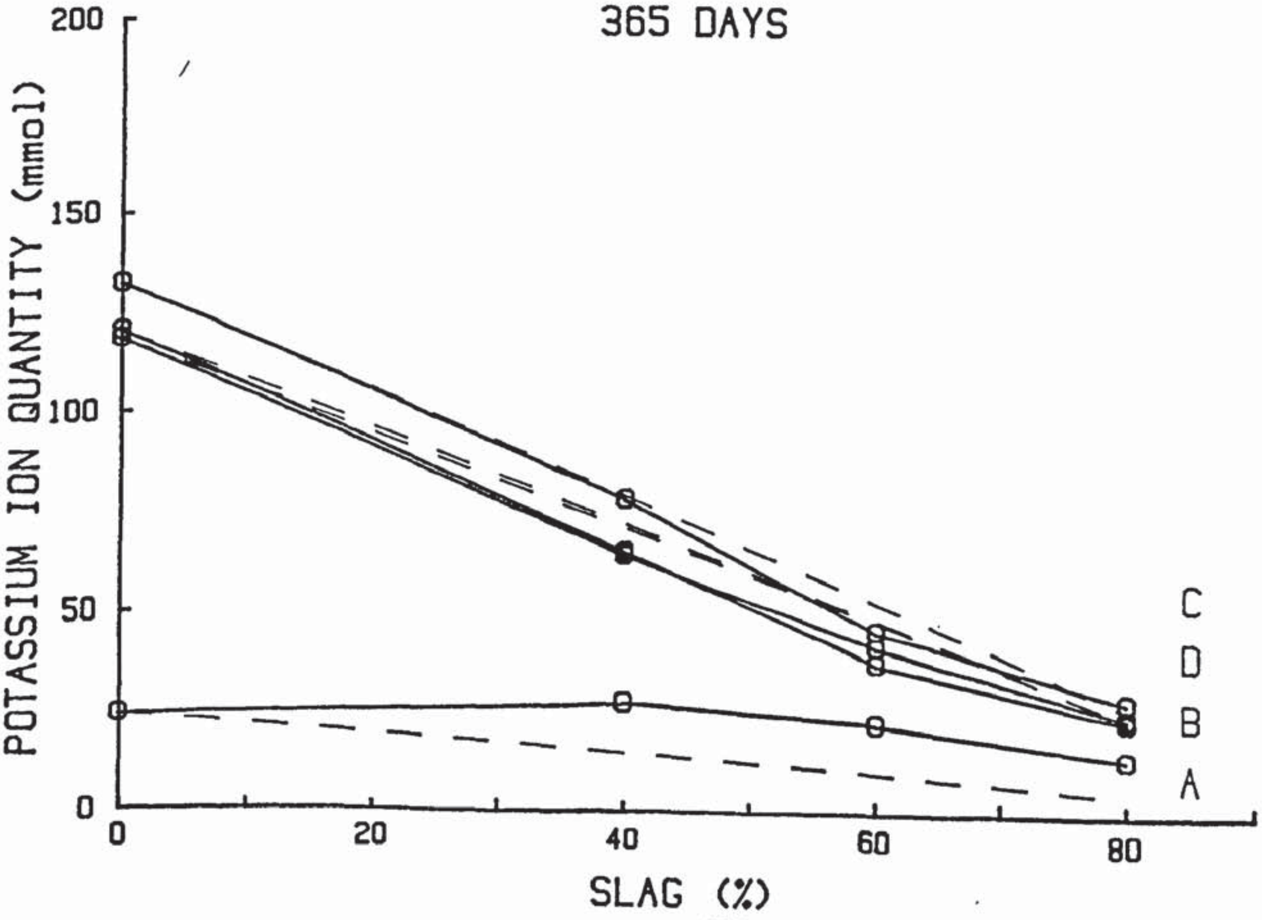


Fig 5.17

Quantity of potassium ions in solution of cements substituted with gbfs

Fig 5.18



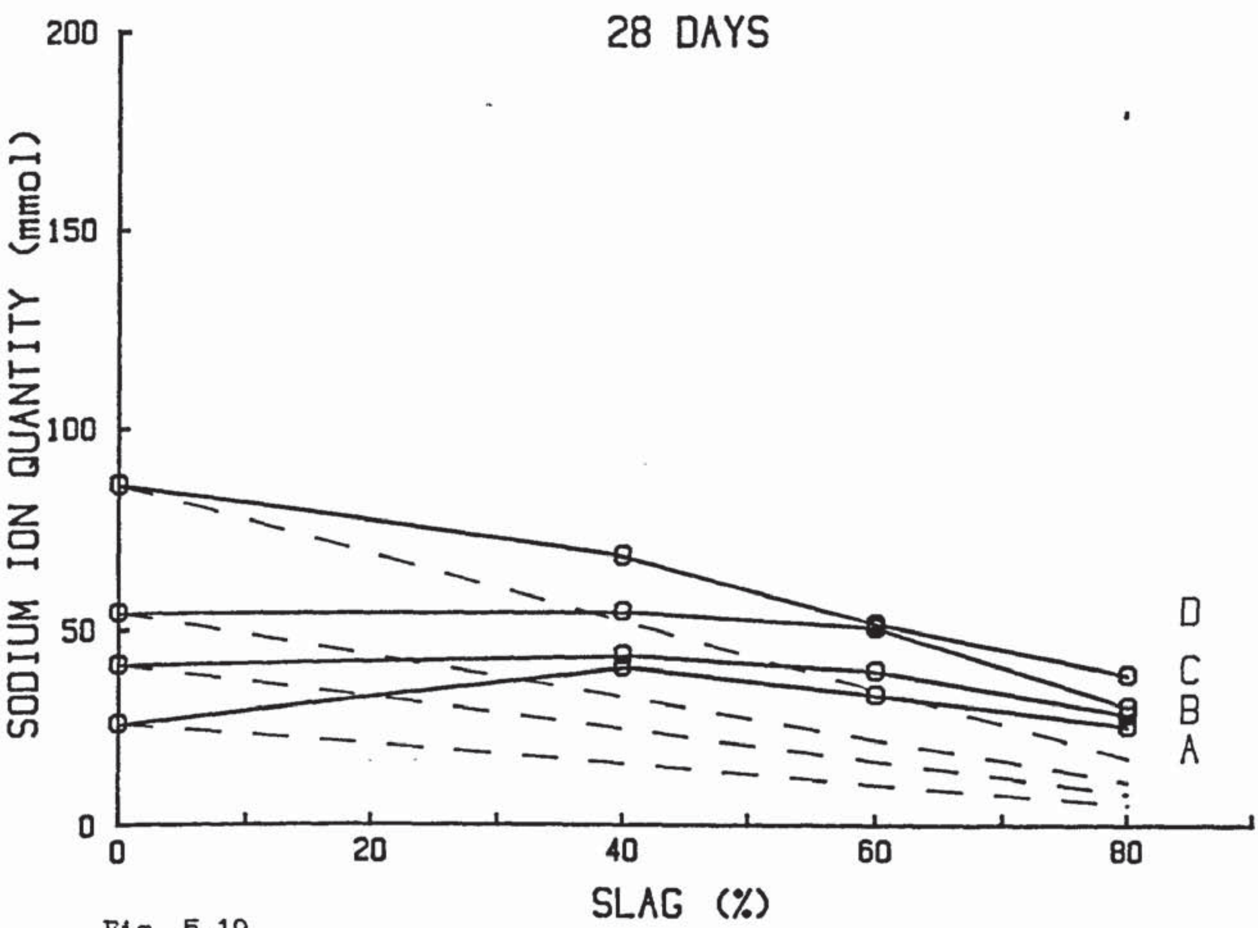
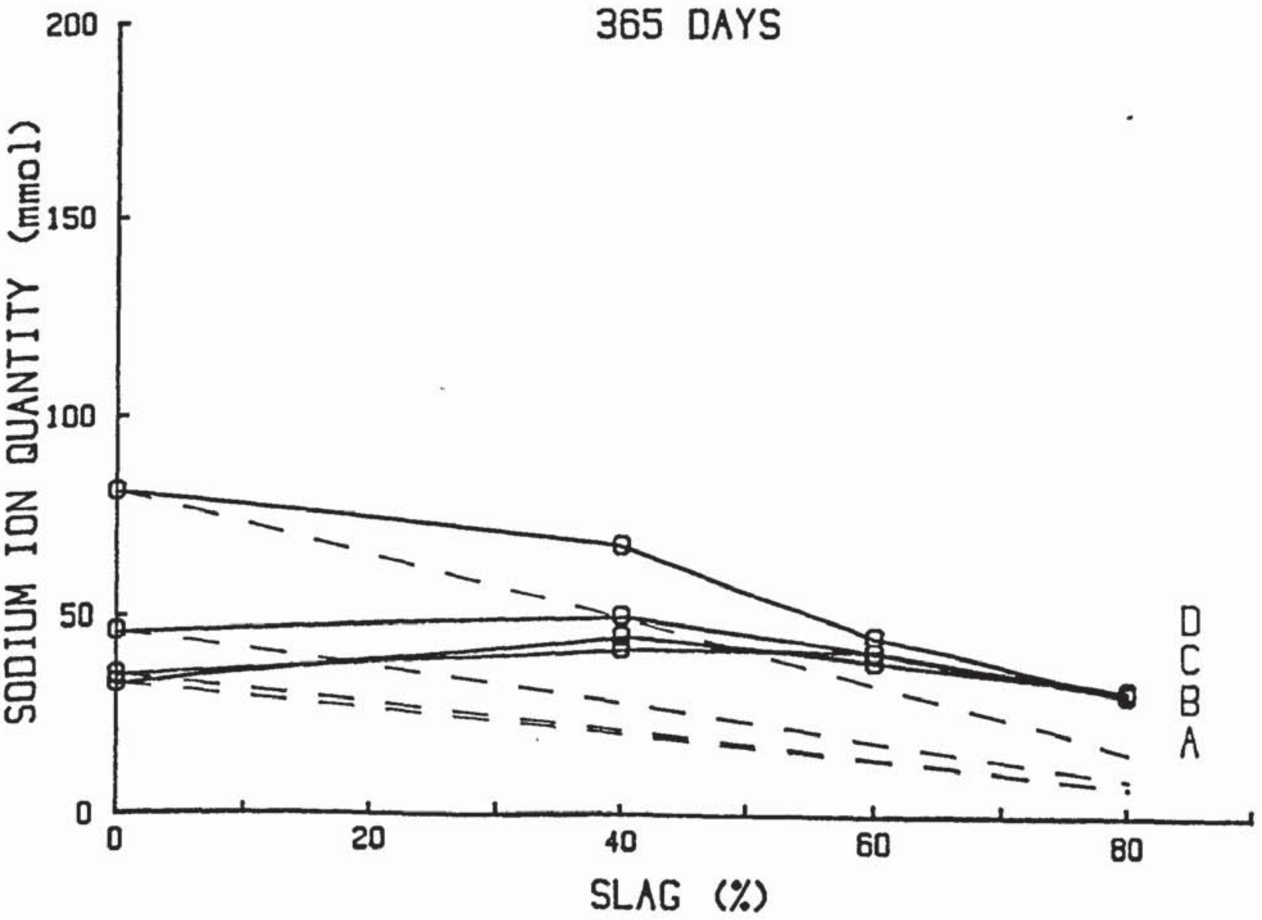


Fig 5.19

Quantity of sodium ions in solution of cements substituted with gbfs

Fig 5.20



Appendix 6

TABLE 6.1 CEMENT B with 20% PFA REPLACEMENT

AGE (days)	PFA	IONIC CONCENTRATIONS mmols/l OH	pH	K	Na	Ve g/g	QTY OF IONS IN SOLN. OH	K	Na	EQ.OH FACTOR Conc.	DILUTION % Qty
28	CONTROL	604	13,78	457	141	0,275	166	126	39		
	2	472	13,67	308	156	0,302	142	93	47	22	14
	3	530	13,72	352	168	0,302	160	106	51	12	4
	4	480	13,68	338	124	0,297	142	100	37	21	14
	5	482	13,68	332	129	0,313	151	104	40	20	9
84	CONTROL	646	13,81	460	152	0,256	165	118	39		
	2	458	13,66	284	177	0,297	136	84	53	29	18
	3	473	13,68	273	166	0,290	137	79	48	29	17
	4	379	13,58	252	98	0,282	107	71	28	41	35
	5	396	13,60	264	99	0,305	121	81	30	39	27
168	CONTROL	661	13,82	472	156	0,253	167	119	39		
	2	442	13,65	255	179	0,295	130	75	53	33	22
	3	453	13,66	271	173	0,280	127	76	48	32	24
	4	331	13,52	205	87	0,275	91	56	24	50	46
	5	337	13,53	219	87	0,489	98	63	25	49	42
365	CONTROL	662	13,82	484	146	0,250	165	121	37		
	2	420	13,62	221	172	0,274	115	61	47	37	31
	3	404	13,61	235	150	0,274	111	64	41	39	33
	4	289	13,46	188	91	0,279	78	51	25	56	53
	5	312	13,49	204	94	0,282	88	58	27	53	47

TABLE 6.2 CEMENT B with 40% PFA REPLACEMENT

AGE (days)	PFA	IONIC CONCENTRATIONS mmols/L				We g/g	QTY OF IONS IN SOLN.			EQ.OH DILUTION FACTOR	%
		OH	pH	K	Na		OH	K	Na	Conc.	Qty
28	CONTROL	604	13,78	457	141	0,275	166	126	39		
	2	360	13,55	199	147	0,315	114	63	46	45	7
	3	387	13,59	228	140	0,318	123	73	45	36	26
	4	316	13,50	202	77	0,313	99	63	24	48	40
	5	330	13,52	207	81	0,318	105	66	26	45	37
84	CONTROL	646	13,81	460	152	0,256	165	118	39		
	2	357	13,55	191	151	0,299	107	57	45	45	36
	3	381	13,58	211	152	0,311	119	66	47	41	28
	4	276	13,44	167	78	0,313	86	52	24	57	48
	5	283	13,45	176	74	0,312	88	55	23	56	47
168	CONTROL	661	13,82	472	156	0,253	167	119	39		
	2	334	13,52	180	154	0,296	99	53	46	50	41
	3	352	13,55	195	154	0,303	107	59	47	47	36
	4	243	13,39	154	78	0,310	75	48	24	63	55
	5	247	13,39	153	77	0,309	76	47	24	63	54
365	CONTROL	662	13,82	484	146	0,250	165	121	37		
	2	320	13,51	165	148	0,287	92	47	42	52	45
	3	326	13,51	166	138	0,300	98	50	41	51	41
	4	199	13,30	122	67	0,304	60	37	20	70	64
	5	236	13,37	143	78	0,300	71	43	23	64	57

Table 6.3 Ions removed by pfa's over experimental period

		Ions Removed by PFA Between 28 and 365 Days					
Cement B Incl PFA.		20%			40%		
	(eq Na_2O)	OH	K	Na	OH	K	Na
PFA 2	(3.37)	26	27	2	11	11	2
PFA 3	(3.20)	48	37	8	24	18	2
PFA 4	(1.04)	63	44	10	38	21	2
PFA 5	(0.97)	62	41	11	33	18	1

Table 6.6 Ions removed by slag's over experimental period

	Ions Removed by Slag Between 28 and 365 Days					
	40%			60%		
	OH	K	Na	OH	K	Na
SLAG 1	+6	+3	+10	10	+1	+1
SLAG 2	15	3	+6	18	9	+2
SLAG 3	7	5	+5	7	0	4

TABLE 6,4 CEMENT B with 40% SLAG

AGE (days)	SLAG	IONIC CONCENTRATIONS mmols/L				We	QTY OF IONS IN SOLN.			EQ.OH DILUTION FACTOR %	
		OH	pH	K	Na	g/g	OH	K	Na	Conc.	Qty
28	CONTROL	604	13,78	457	141	0,275	166	126	39		
	1	466	13,67	251	147	0,281	131	71	41	23	21
	2	384	13,58	249	107	0,275	105	68	29	37	37
	3	414	13,62	249	140	0,284	118	71	40	32	29
84	CONTROL	646	13,81	460	152	0,256	165	118	39		
	1	496	13,70	257	159	0,281	139	72	45	23	16
	2	391	13,59	230	128	0,285	112	66	36	39	33
	3	433	13,64	250	166	0,289	125	72	48	33	24
168	CONTROL	661	13,82	472	156	0,252	167	119	39		
	1	484	13,69	243	150	0,291	141	71	44	27	16
	2	368	13,57	189	129	0,279	103	53	33	44	39
	3	428	13,63	235	150	0,286	122	67	43	35	27
365	CONTROL	662	13,82	484	146	0,250	165	121	37		
	1	506	13,70	255	181	0,269	136	69	49	24	18
	2	323	13,51	177	118	0,276	89	49	33	51	46
	3	415	13,62	229	161	0,266	110	61	43	37	33

TABLE 6,5

CEMENT B with 60% SLAG

AGE (days)	SLAG	IONIC CONCENTRATIONS mmols/L OH	pH	K	Na	We g/g	QTY OF IONS IN SOLN. OH	K	Na	EQ.OH DILUTION FACTOR Conc.	% Qty
28	CONTROL	604	13,78	457	141	0,275	166	126	39		
	1	341	13,53	166	141	0,317	108	53	41	44	35
	2	250	13,40	133	89	0,317	79	42	29	59	52
	3	297	13,47	143	141	0,311	92	44	44	51	44
84	CONTROL	646	13,81	460	152	0,256	165	118	39		
	1	339	13,53	166	145	0,296	100	49	43	48	40
	2	242	13,30	127	98	0,313	76	40	29	63	54
	3	285	13,45	124	136	0,309	88	38	42	56	47
168	CONTROL	661	13,82	472	156	0,252	167	119	39		
	1	341	13,53	171	150	0,290	99	50	44	49	41
	2	232	13,37	106	87	0,314	73	33	27	65	56
	3	286	13,46	127	134	0,307	88	39	41	57	48
365	CONTROL	662	13,82	484	146	0,250	165	121	37		
	1	359	13,56	180	163	0,270	97	49	44	46	41
	2	192	13,28	91	89	0,310	60	28	28	71	64
	3	287	13,46	135	161	0,292	84	39	38	57	49

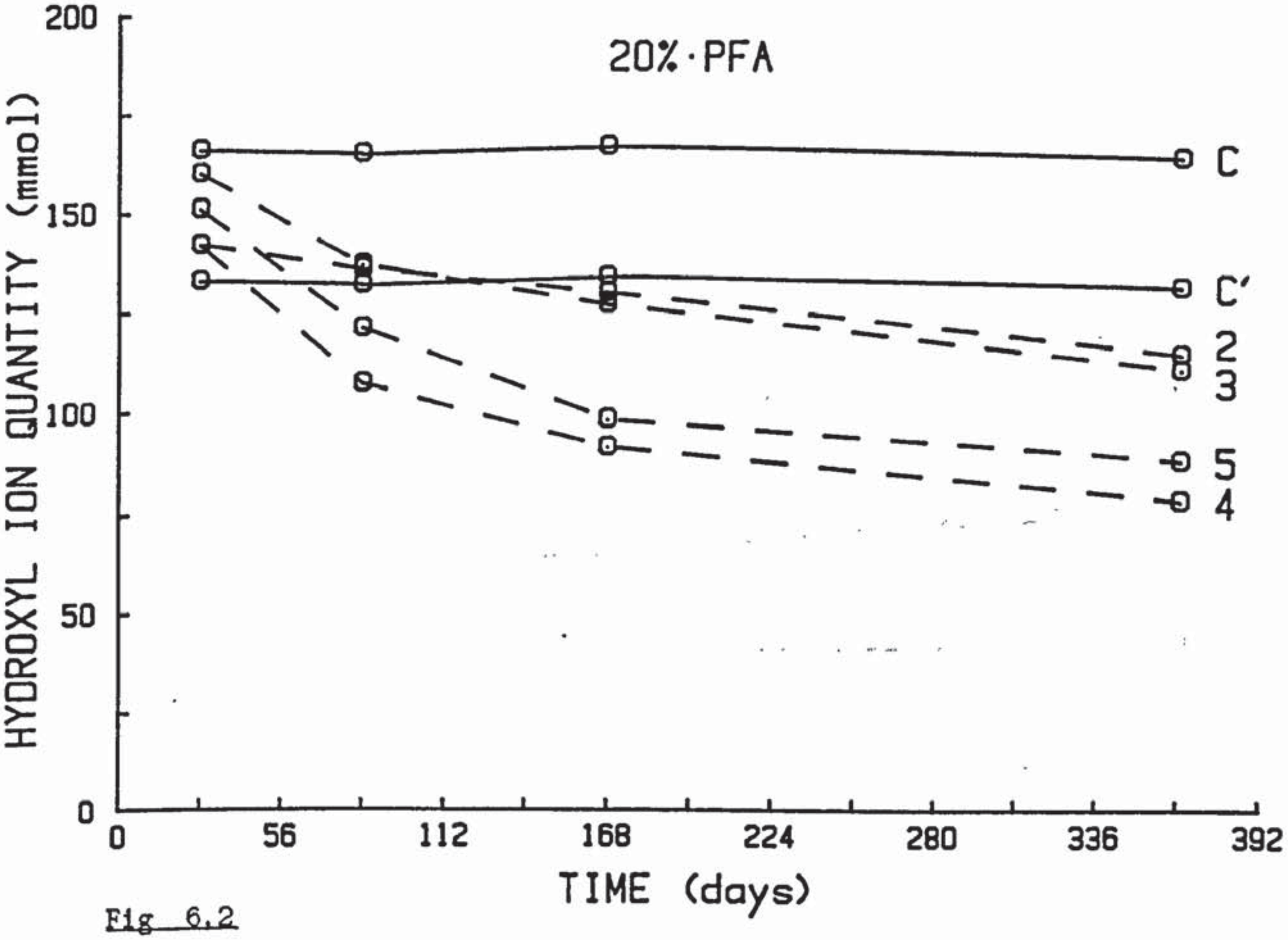
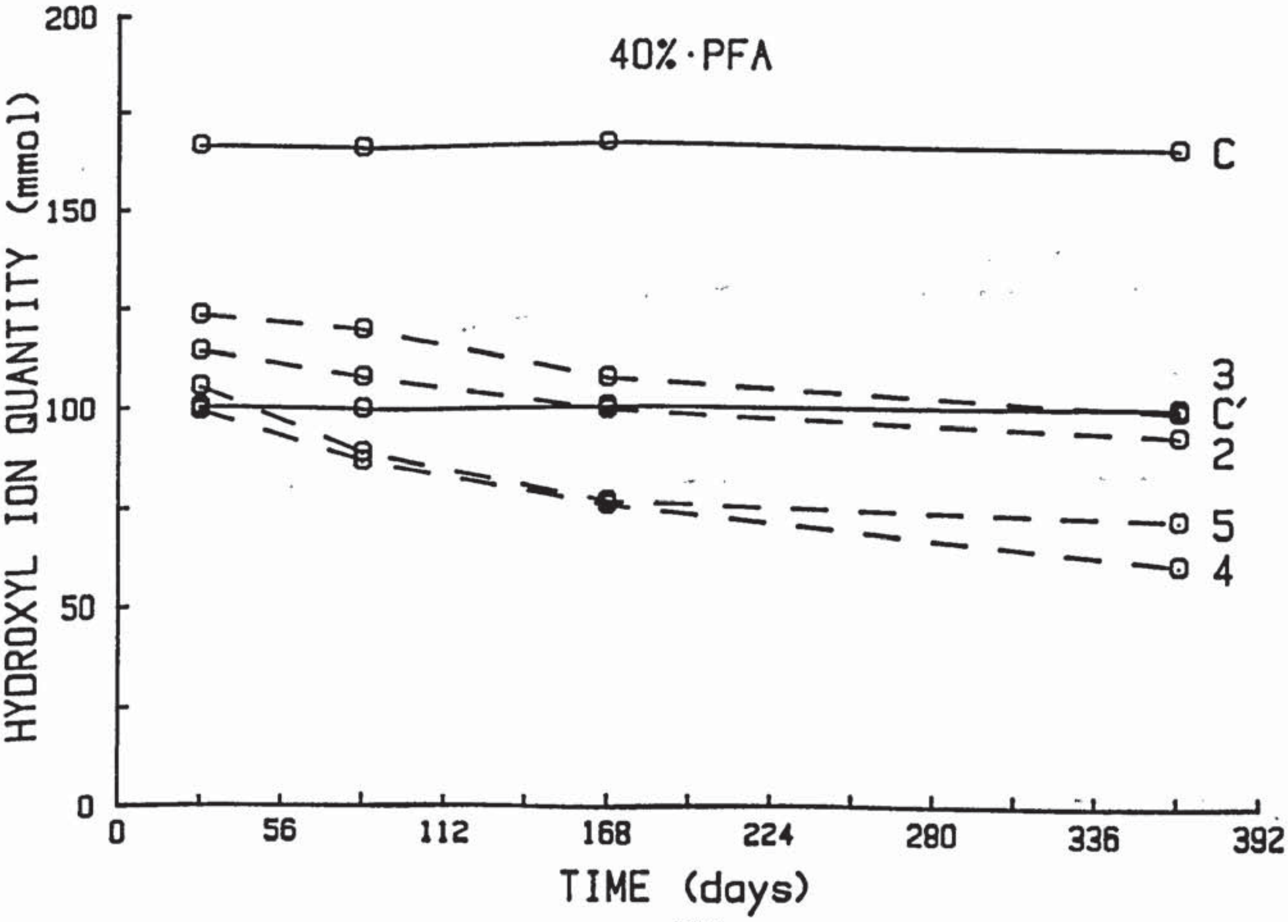


Fig 6.2

Quantity of OH ions in solution as a function of time

Fig 6.3



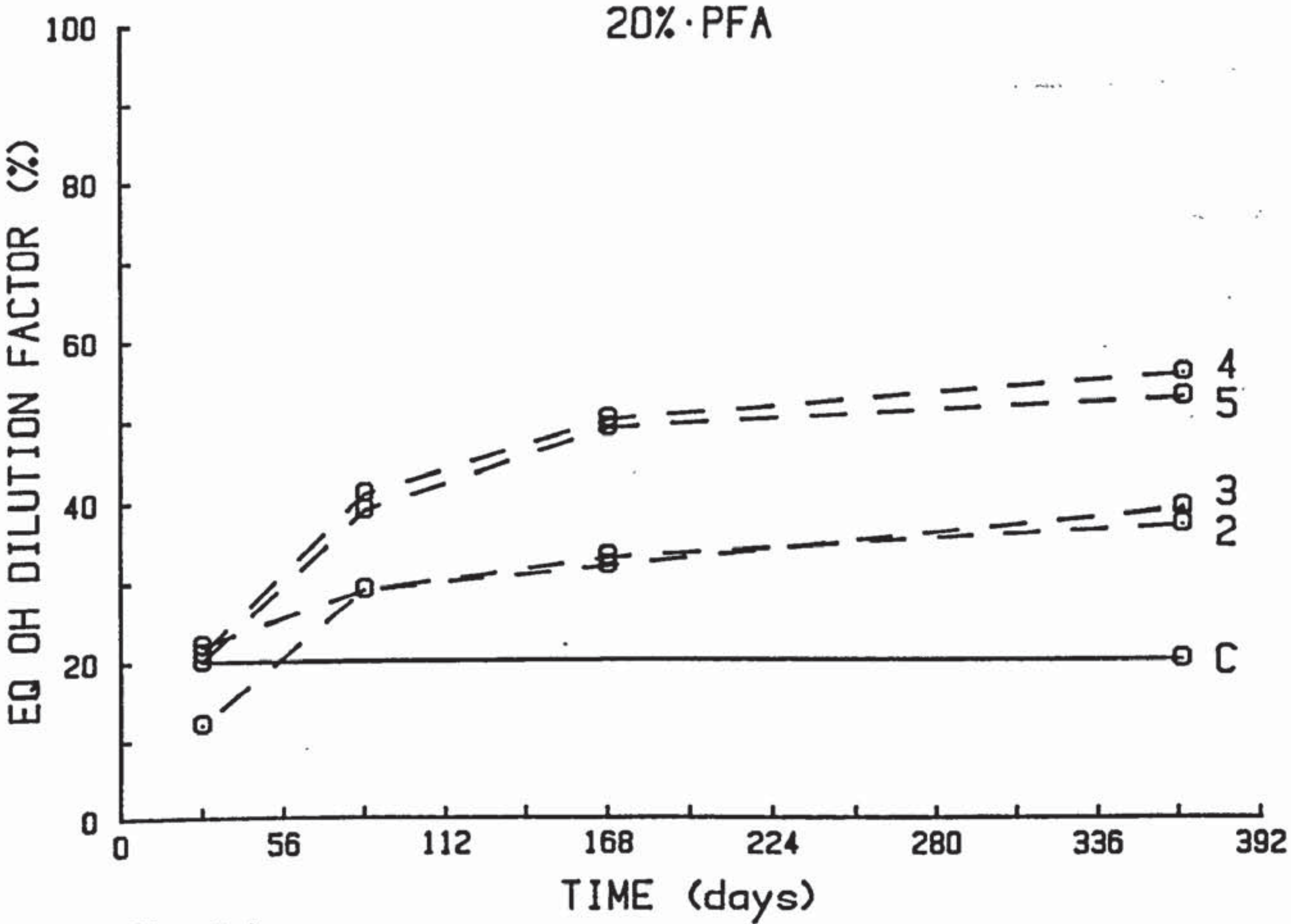
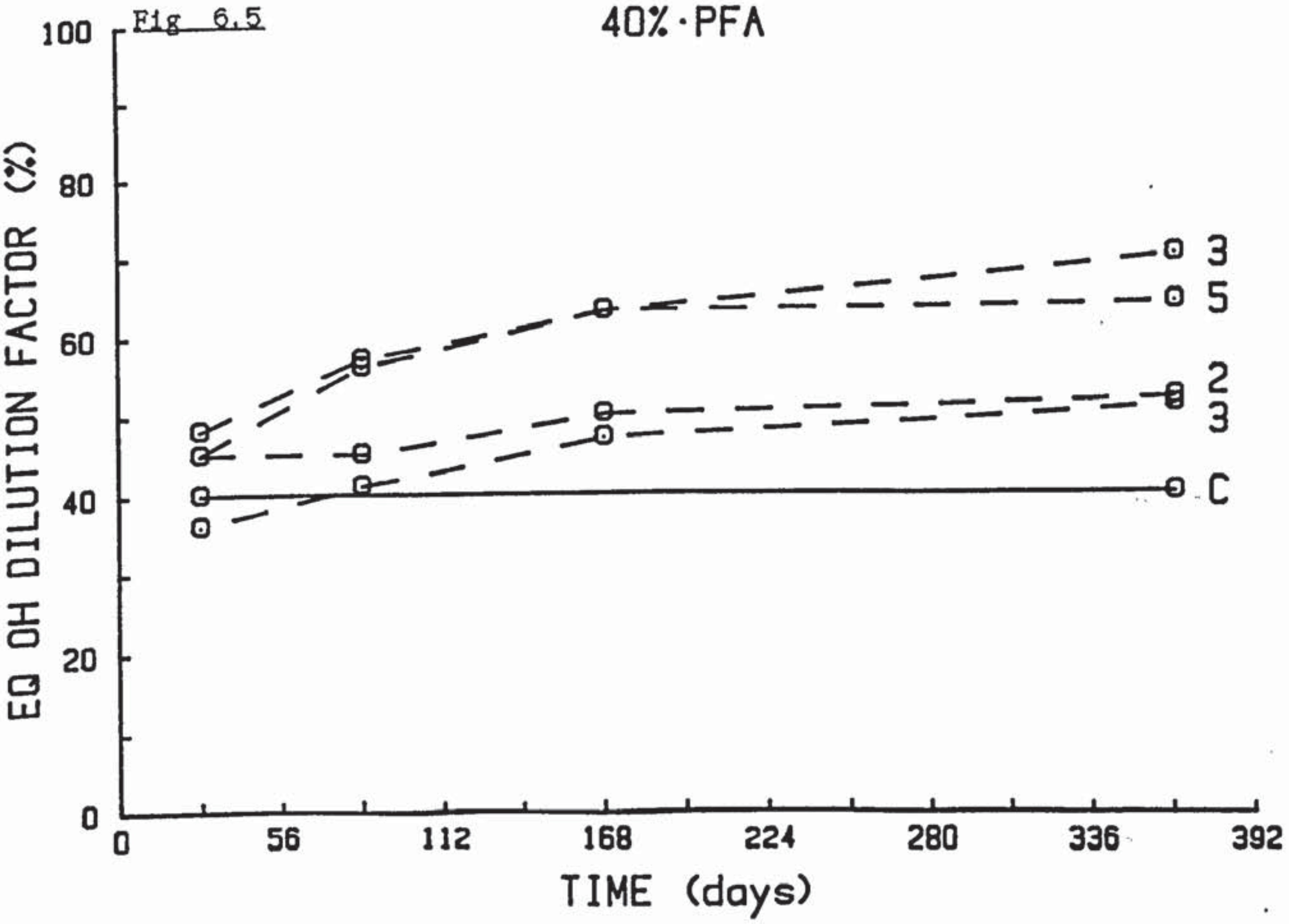


Fig 6.4

Equivalent OH dilution factor (concentration) as a function of time

Fig 6.5



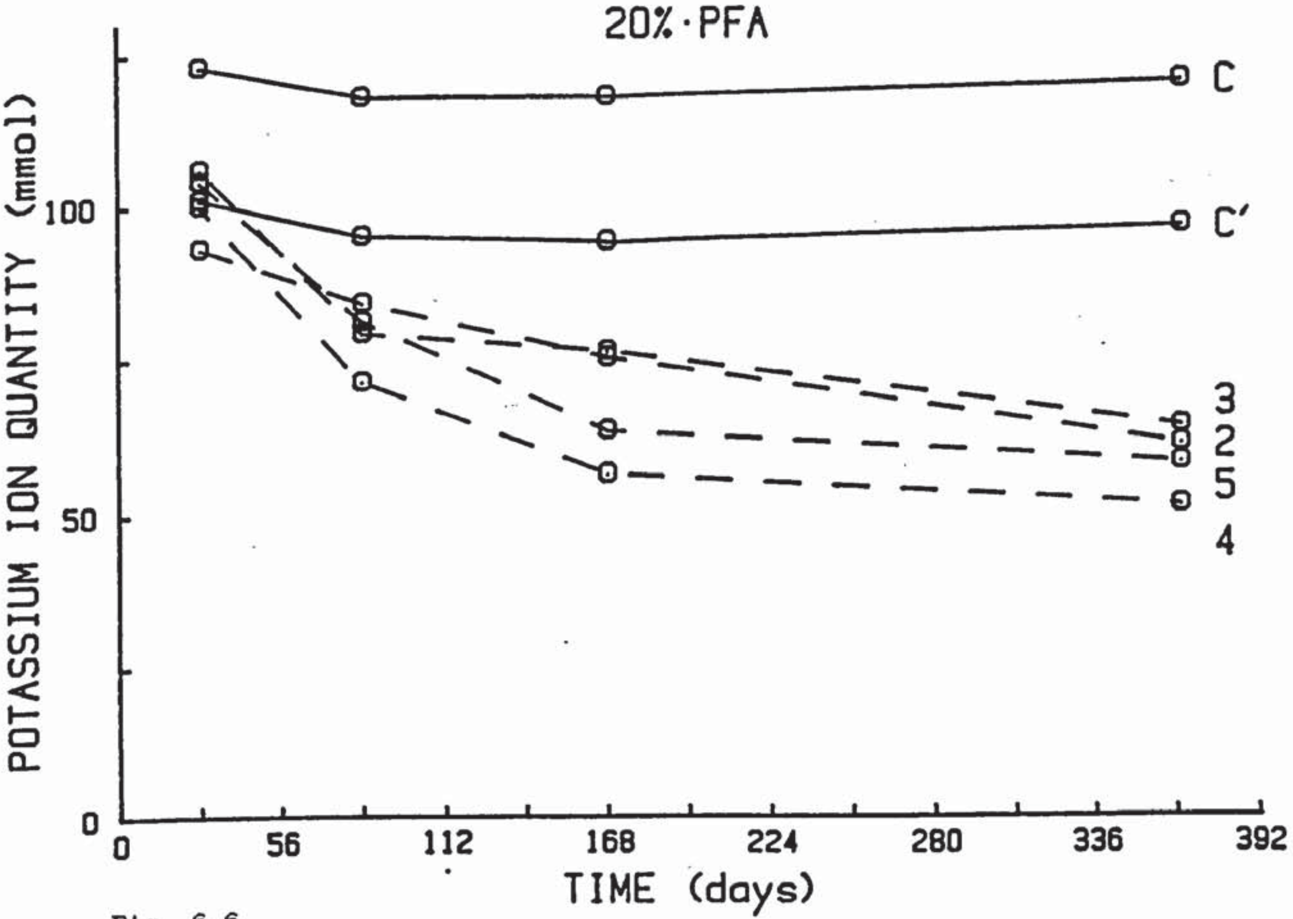
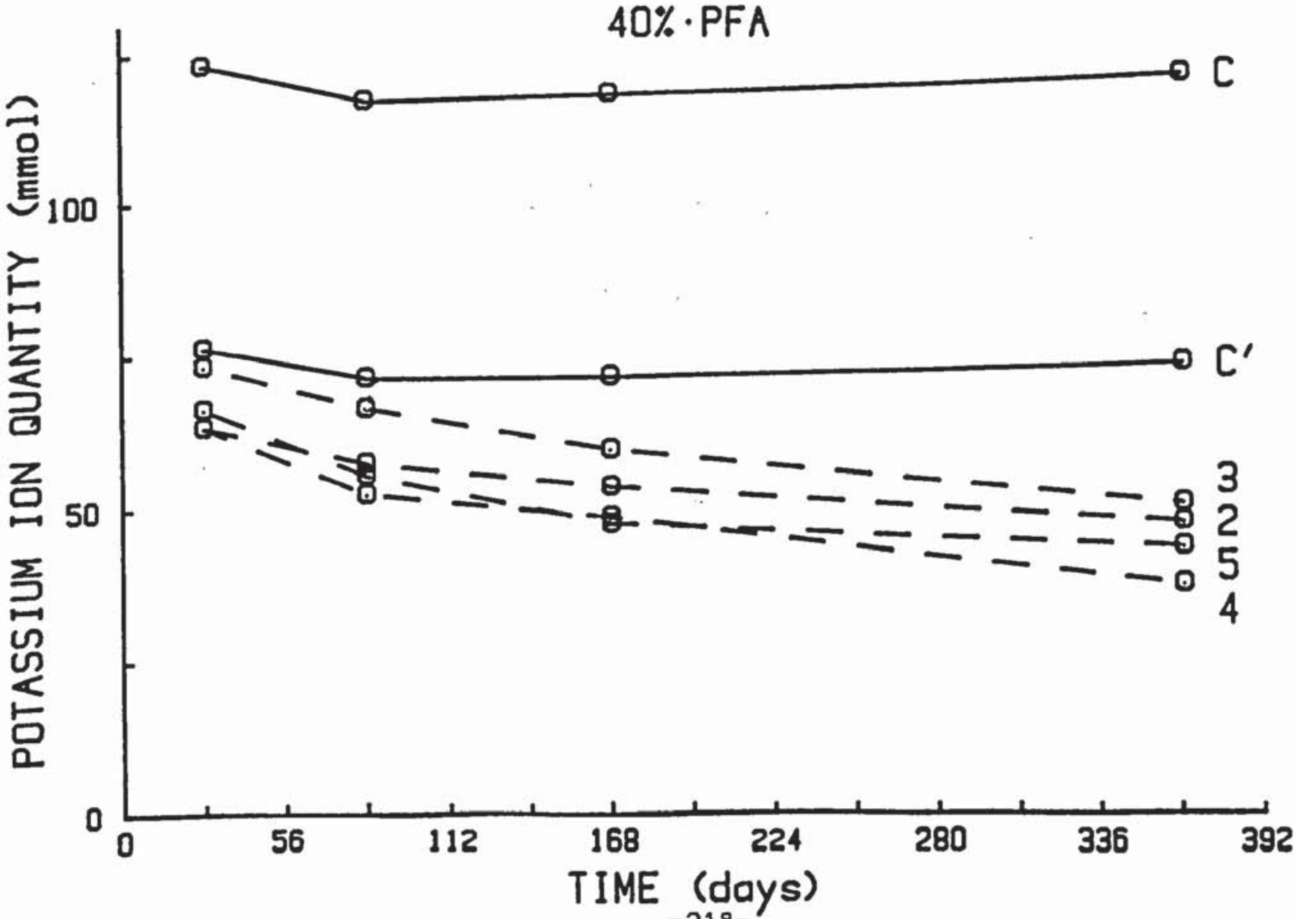


Fig 6.6

Quantity of K ions in solution as a function of time

Fig 6.7



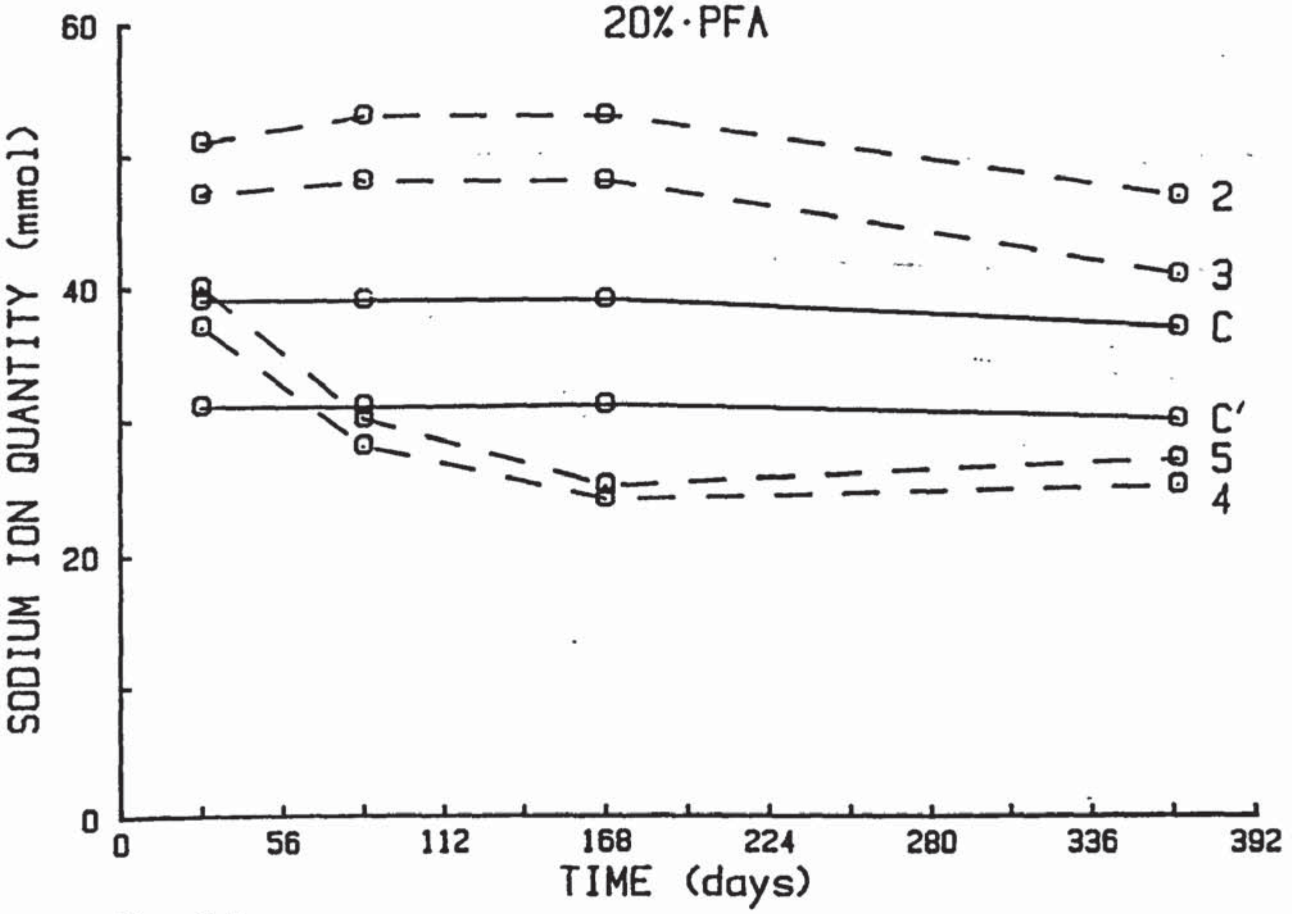
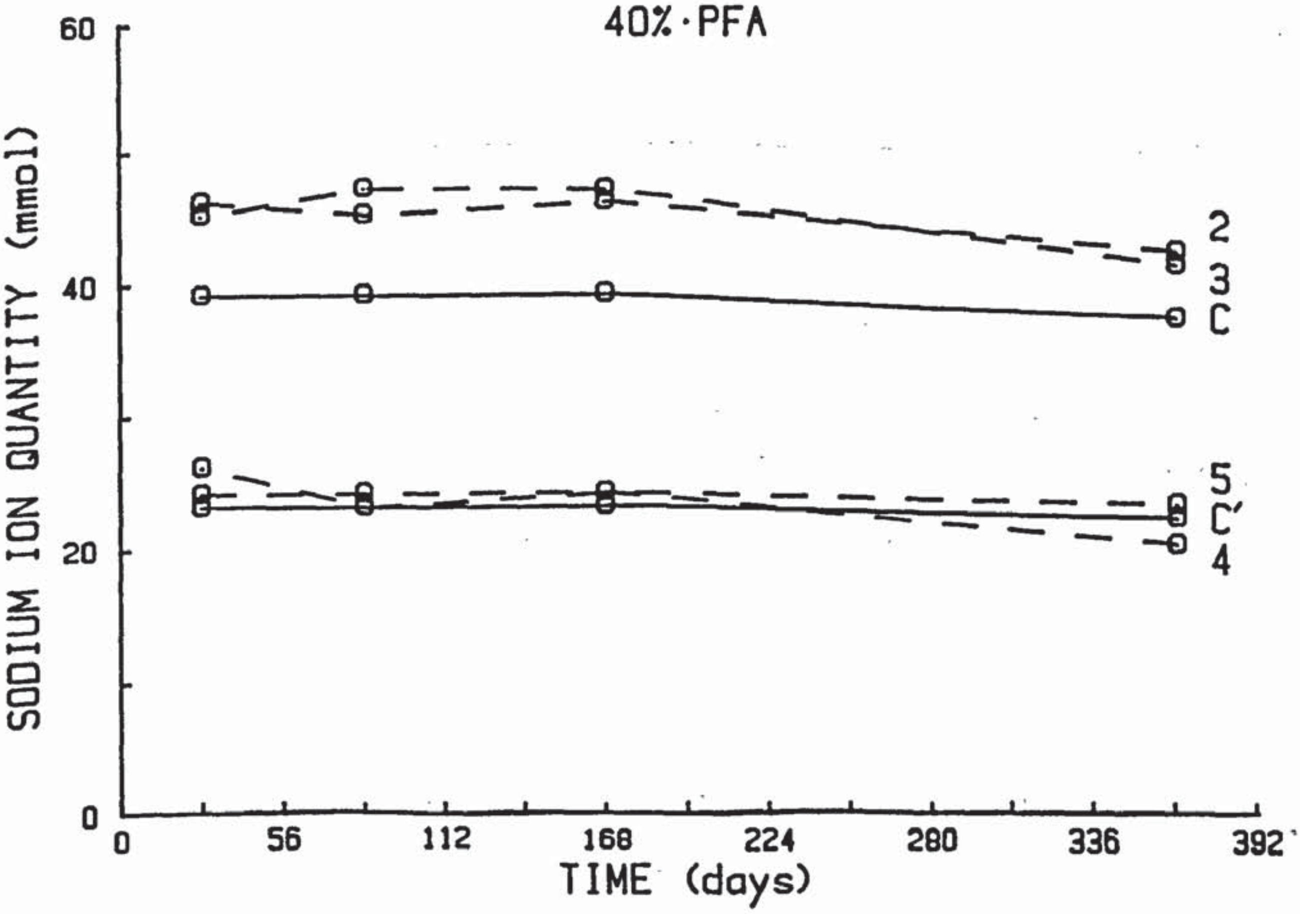


Fig 6.8

Quantity of Na ions in solution as a function of time

Fig 6.9



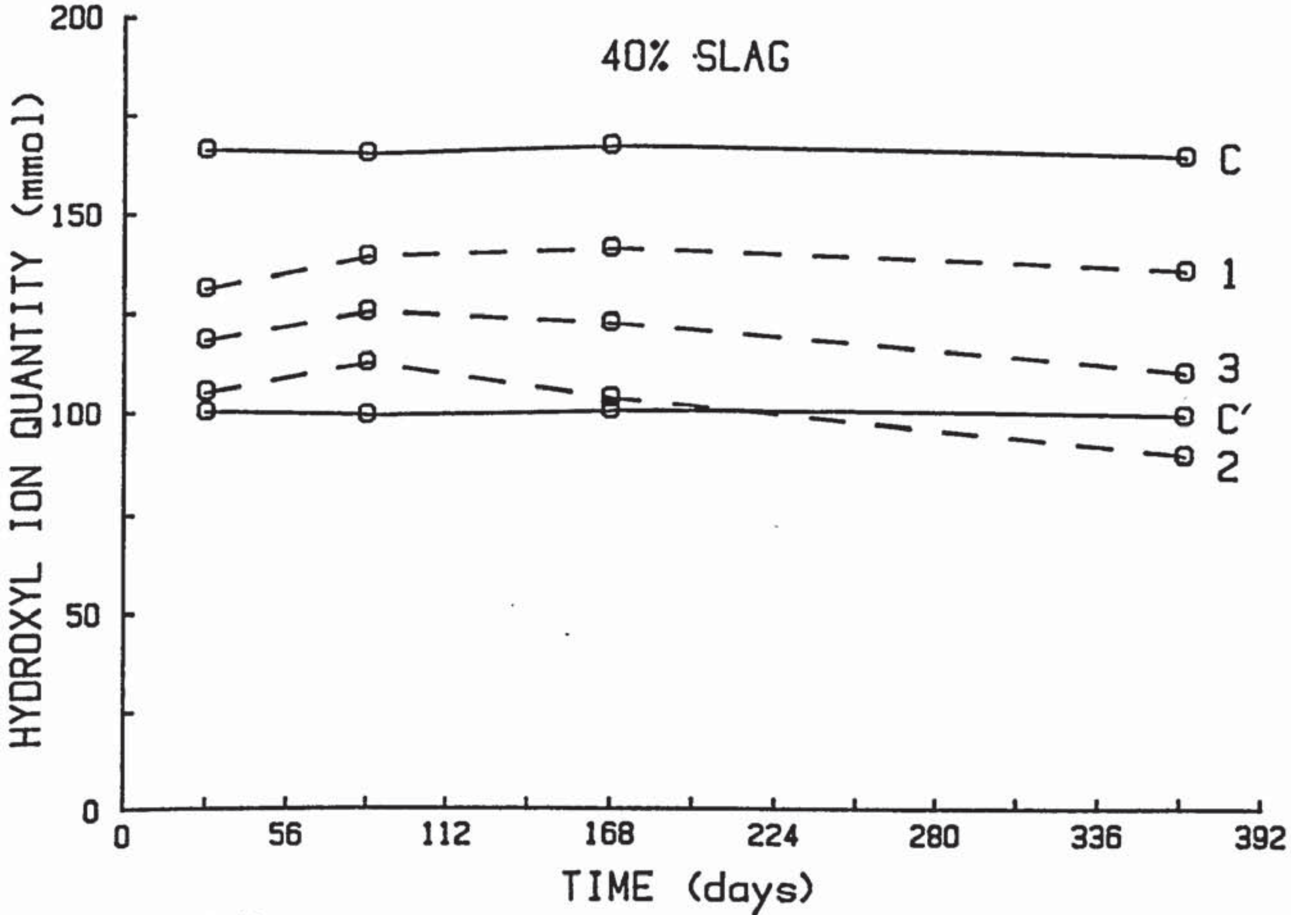
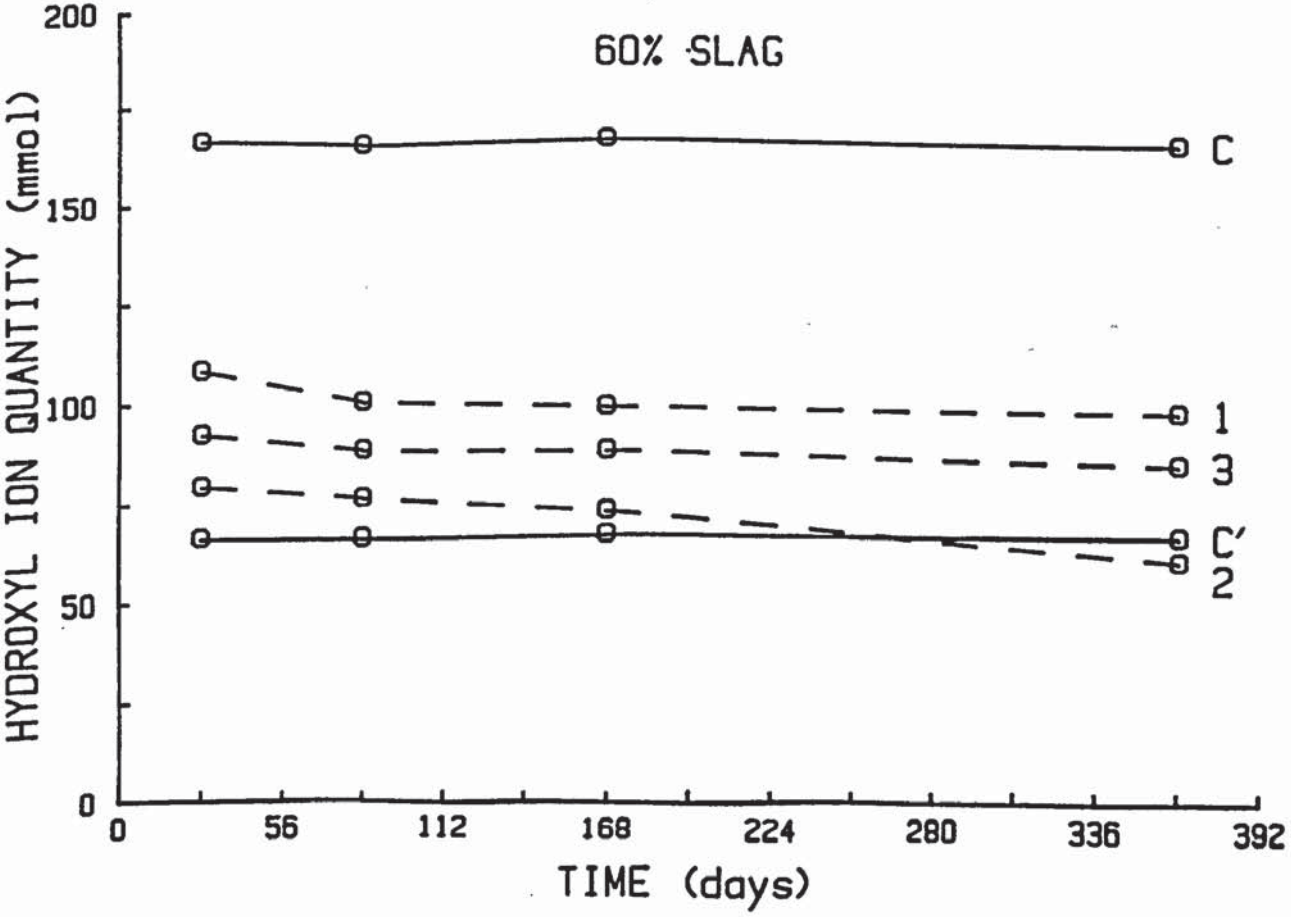


Fig 6.10

Quantity of OH ions in solution as a function of time

Fig 6.11



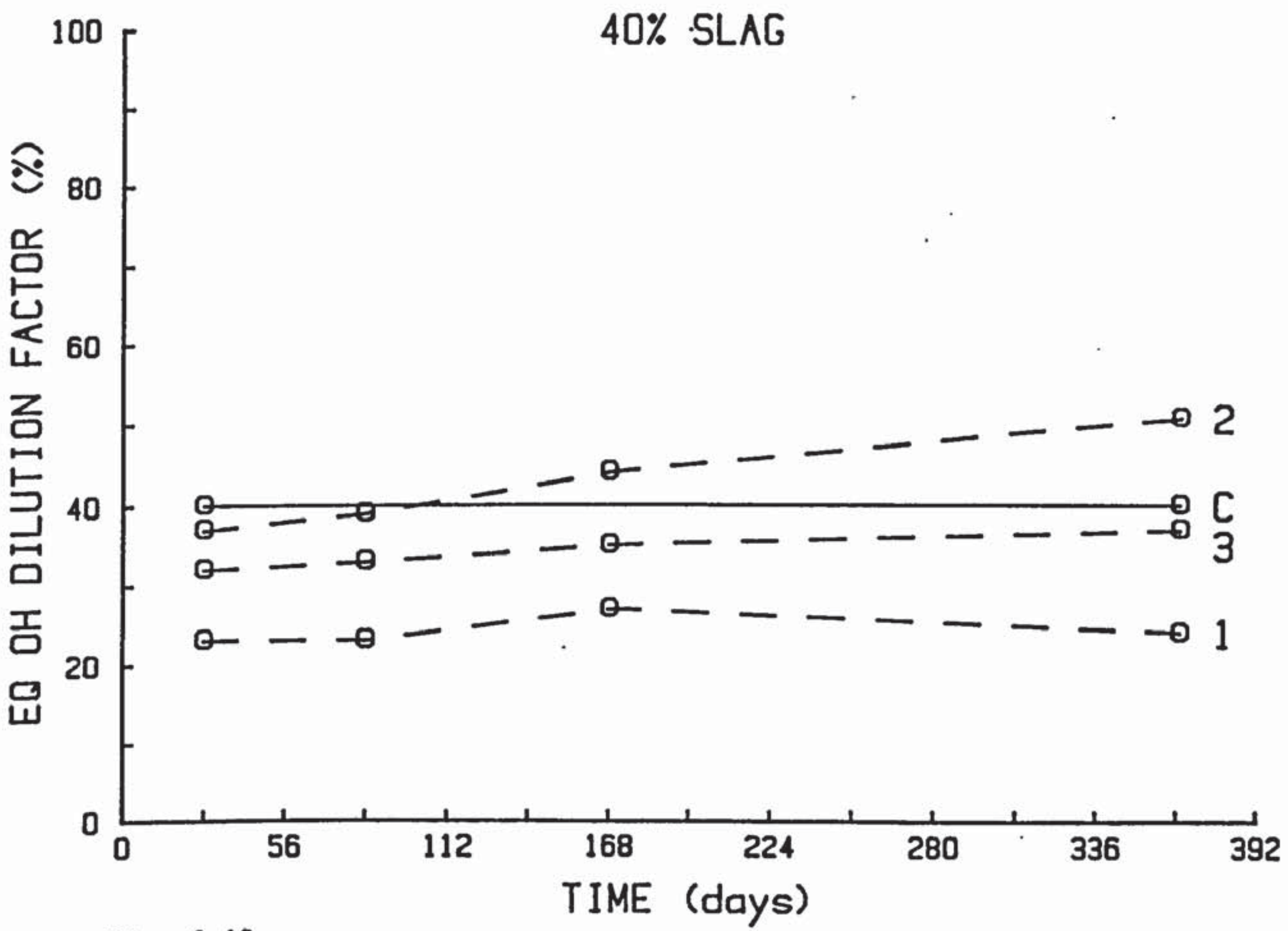
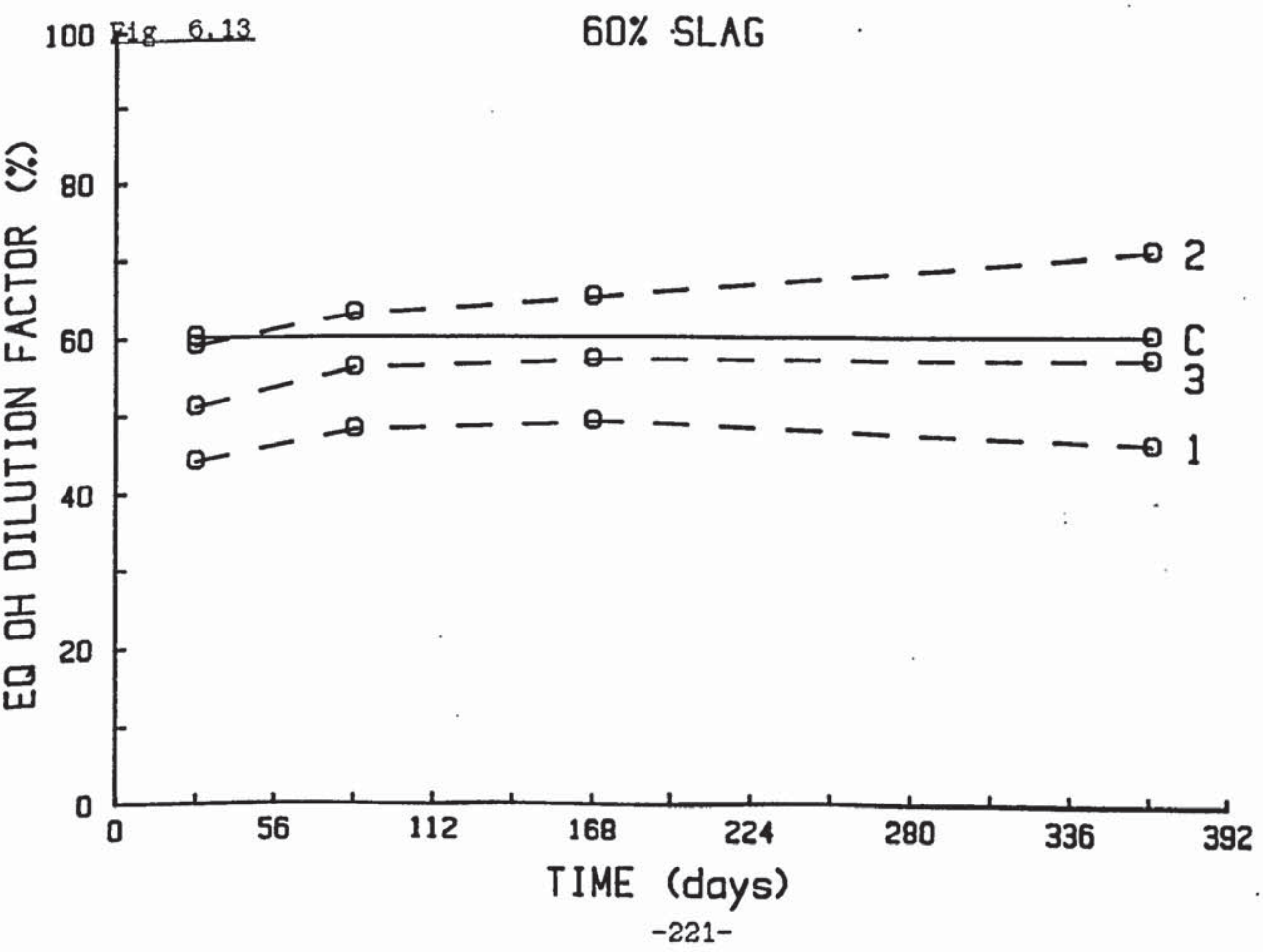


Fig 6.12

Equivalent OH dilution factor (concentration) as a function of time

Fig 6.13



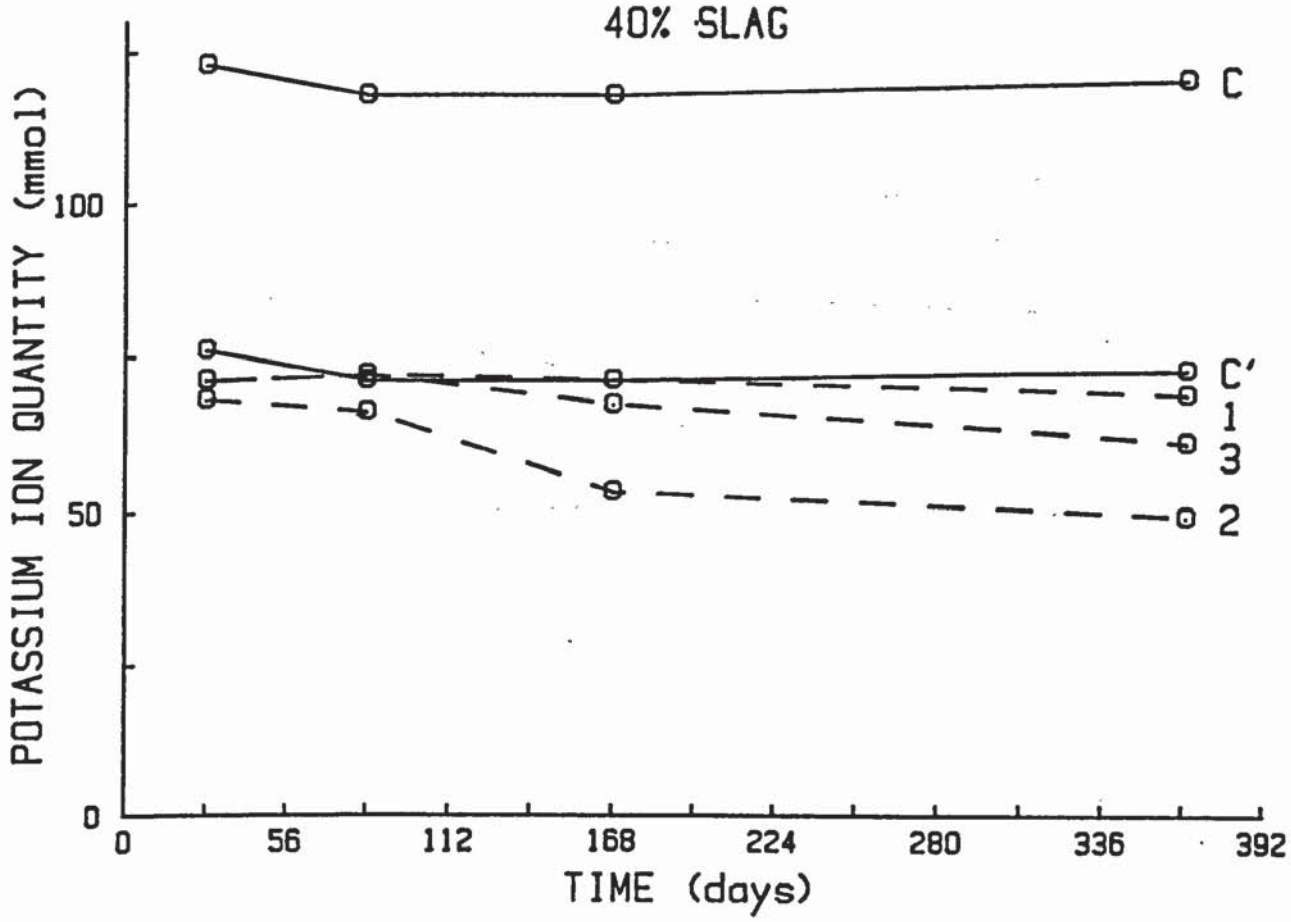
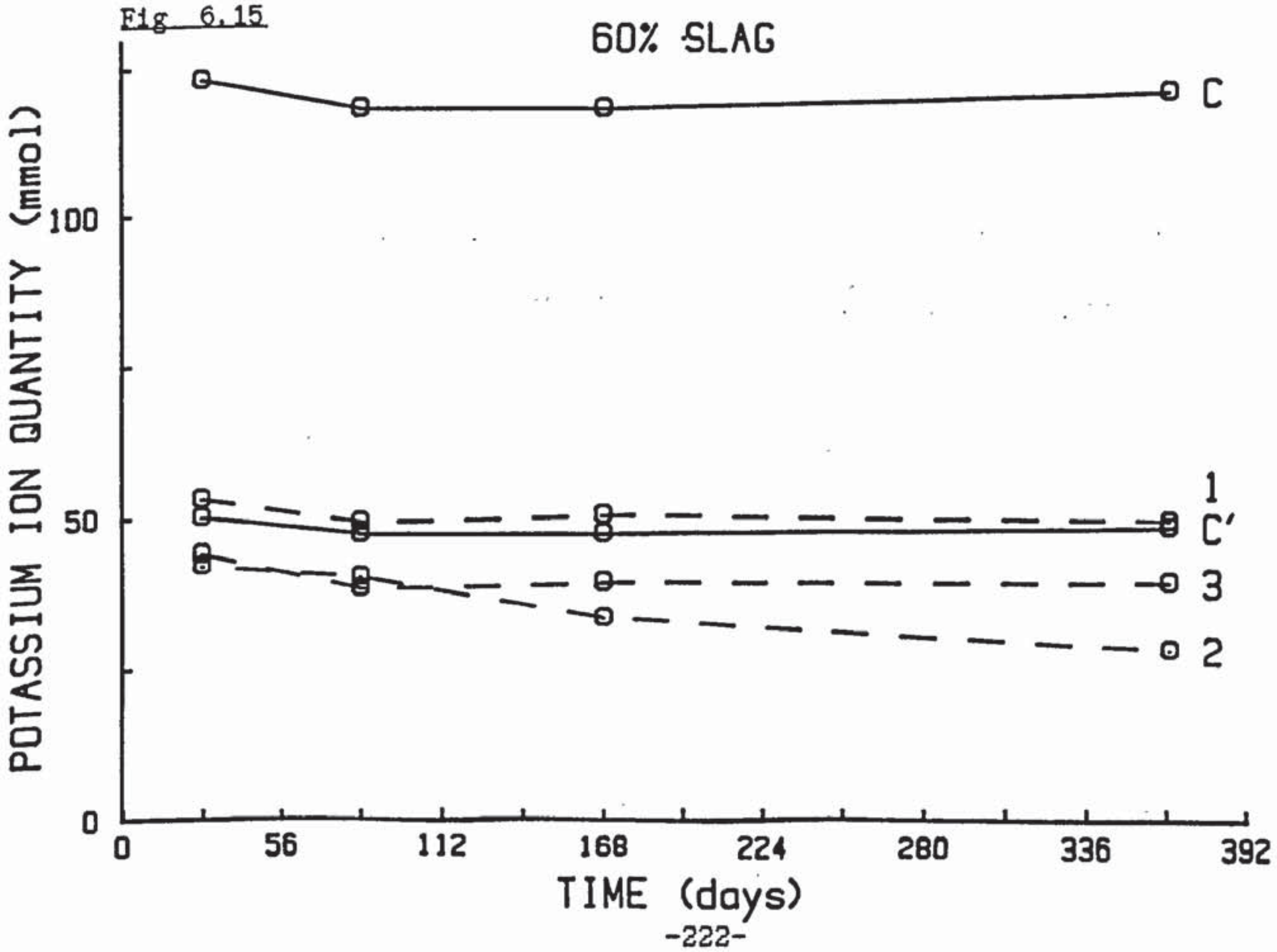


Fig 6.14

Quantity of K ions in solution as a function of time

Fig 6.15



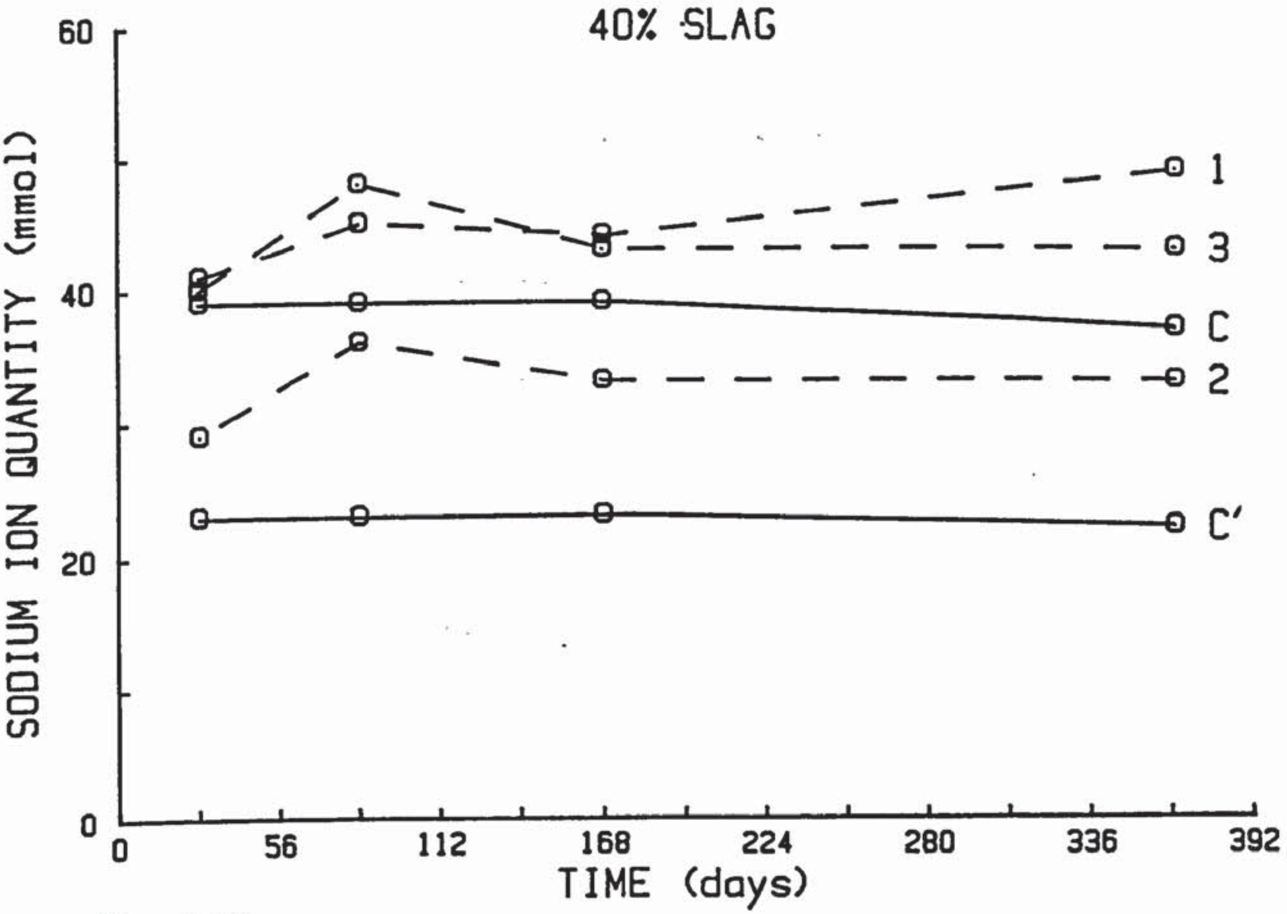
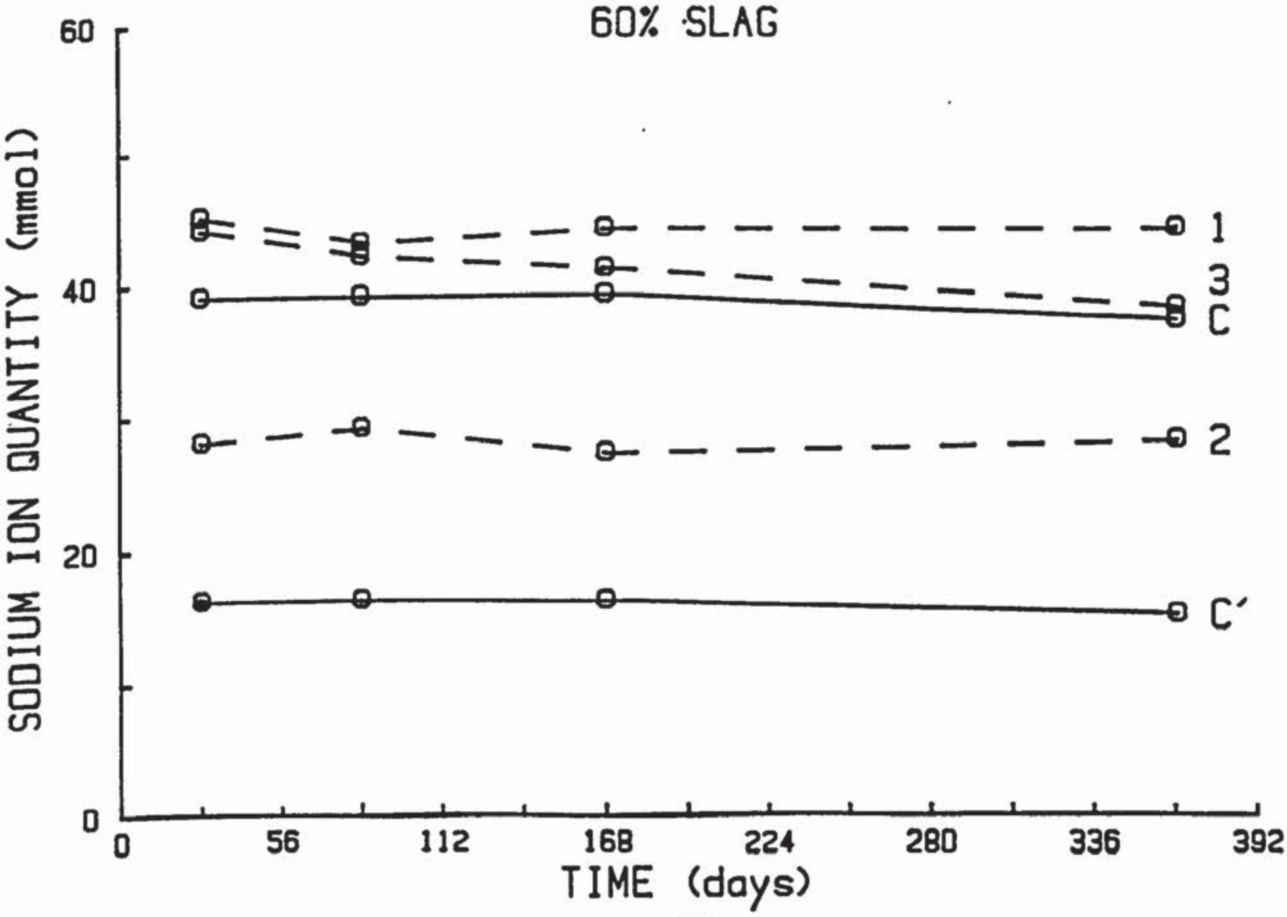


Fig 6.16

Quantity of Na ions in solution as a function of time

Fig 6.17



APPENDIX 7

Calculation of Alkali required (per gramme of cement) to reproduce design alkali levels

1. Establish the quantity of alkali required.

ΔNa_2O = Design alkali content - Base cement alkali content (grammes Na_2O eq)

2. Conversion of alkali required from Na_2O to NaCl

$$\text{NaCl required} = \frac{MW\ (NaCl)}{AW\ (Na)} \times \frac{AW\ (Na_2)}{MW\ (Na_2O)}$$

(grammes NaCl)

2A. For SSW calculation only.
Convert alkali required from Na_2O to SSW (having a NaCl content of 61%)

$$\text{SSW required} = \frac{NaCl}{Na \times 0.61} \times \frac{Na_2}{1\ Na_2O} \times \Delta Na_2O$$

(grammes SSW powder)

Example

Calculation of alkali salts required (per grammes of cement) to be added to cement B to achieve an alkali content equivalent of cement E.

1. $\Delta Na_2O = 0.0106 - 0.0067 = 0.0039$ grammes

2. $\text{NaCl required} = \frac{58.5}{23} \times \frac{46}{62} \times 0.0039 = 0.0074$ grammes

2A. $\text{SSW required} = \frac{58.5}{23 \times 0.6162} \times \frac{46}{62} \times 0.0039 = 0.0121$ grammes

Appendix 7

TABLE 7.1 DATA FOR SPECIMENS CURED FOR 28 DAYS AT 20°C.

CEMENT EQUIV.	IONIC CONCENTRATIONS mmols/l					Ve	QTY OF IONS IN SOLN mmols/g			
	OH	pH	Cl	K	Na	g.	OH	Cl	K	Na
B	605	13,78	6	530	97	0,313	189	2	166	30
C	650	13,81	7	563	108	0,319	207	2	180	34
D	744	13,87	5	558	226	0,315	234	2	176	71
E	808	13,91	3	564	215	0,319	258	1	180	69
B+NaCl	617	13,79	13	460	163	0,312	193	4	144	51
C	656	13,82	22	474	282	0,314	206	7	149	89
D	690	13,84	34	478	334	0,320	221	11	153	107
E	793	13,90	52	428	440	0,322	255	17	138	142
B+SSV	693	13,84	18	359	270	0,324	225	6	116	87
C	749	13,87	46	350	398	0,341	255	16	119	136
D	833	13,92	76	350	531	0,320	267	24	112	170
E	868	13,94	121	333	657	0,331	287	40	110	217

TABLE 7.2 DATA FOR SPECIMENS CURED FOR 56 DAYS AT 20°C.

CEMENT EQUIV.	IONIC CONCENTRATIONS mmols/l OH	pH	Cl	K	Na	Ve g.	QTY OF IONS IN SOLN mmols/g OH	Cl	K	Na
B	661	13,82	2	539	98	0,287	190	1	155	28
C	690	13,83	2	578	112	0,289	199	1	167	32
D	752	13,88	2	521	197	0,312	235	1	163	61
E	837	13,92	1	570	210	0,309	259	0	176	65
B+NaCl	617	13,79	11	450	200	0,310	191	3	140	62
C	672	13,83	18	470	269	0,309	208	6	145	83
D	710	13,85	28	478	364	0,312	222	9	149	114
E	822	13,93	33	430	441	0,316	260	0	136	139
B+SSW	706	13,85	16	371	286	0,314	222	5	116	90
C	767	13,89	43	385	440	0,297	228	13	114	131
D	839	13,92	76	353	566	0,306	257	23	108	173
E	890	13,95	136	346	659	0,320	285	44	111	211

TABLE 7.3 DATA FOR SPECIMENS CURED FOR 84 DAYS AT 20°C.

CEMENT EQUIV.	IONIC CONCENTRATIONS mmols/l					Ve	QTY OF IONS IN SOLN mmols/g			
	OH	pH	Cl	K	Na	g.	OH	Cl	K	Na
B	692	13,84	2	551	104	0,270	187	1	149	28
C	692	13,84	1	584	121	0,275	190	0	161	33
D	761	13,88	1	501	202	0,302	230	0	151	61
E	851	13,93	1	578	209	0,295	251	0	171	62
B+NaCl	634	13,80	10	464	202	0,295	187	3	137	60
C	676	13,83	20	481	271	0,293	198	6	141	79
D	718	13,86	28	488	363	0,300	215	8	146	109
E	845	13,93	40	436	446	0,297	251	12	129	132
B+SSW	720	13,86	18	380	296	0,300	216	5	114	89
C	781	13,89	48	385	440	0,294	230	14	113	129
D	856	13,93	86	374	574	0,285	244	25	107	164
E	879	13,95	135	363	679	0,305	268	41	111	207

TABLE 7,4 DATA FOR SPECIMENS CURED FOR 168 DAYS AT 20º C,

CEMENT EQUIV,	IONIC CONCENTRATION mmols/l					We	QTY OF IONS IN SOLN mmols/g			
	OH	pH	Cl	K	Na	g/g	OH	Cl	K	Na
B	673	13,83	2	562	110	0,260	175	1	146	29
C	683	13,83	4	591	125	0,260	178	1	154	33
D	792	13,90	3	521	209	0,285	226	1	148	60
E	847	13,93	3	587	207	0,285	241	1	167	59
B+NaCl	665	13,82	12	488	210	0,285	190	3	139	60
C	677	13,83	20	473	279	0,283	192	7	134	79
D	725	13,86	30	488	328	0,282	204	8	138	92
E	793	13,90	47	437	418	0,292	232	14	128	122
B+SSW	724	13,86	17	379	297	0,295	214	5	112	88
C	798	13,90	49	382	451	0,280	221	14	107	126
D	843	13,93	71	385	588	0,278	234	20	107	163
E	878	13,84	120	381	699	0,295	259	35	112	206

TABLE 7,5 DATA FOR SPECIMENS CURED FOR 504 DAYS AT 20° C,

CEMENT EQUIV,	IONIC CONCENTRATION mmols/l,					We	QTY OF IONS IN SOLN mmols/g			
	OH	pH	Cl	K	Na	g/g	OH	Cl	K	Na
B	692	13,84	3	580	117	0,245	175	1	142	29
C	708	13,85	1	617	130	0,246	174	0	152	32
D	816	13,91	1	530	214	0,270	220	0	143	58
E	868	13,94	5	592	209	0,274	238	1	162	57
B+NaCl	696	13,84	8	494	216	0,270	188	2	133	58
C	709	13,85	17	492	285	0,275	195	5	135	78
D	751	13,88	31	500	341	0,267	201	8	134	91
E	818	13,91	56	451	430	0,270	221	15	122	116
B+SSW	751	13,88	20	389	303	0,278	209	6	108	84
C	808	13,91	54	389	459	0,271	219	15	105	124
D	866	13,94	73	387	590	0,268	232	20	104	158
E	918	13,96	139	393	739	0,277	254	39	109	205

TABLE 7.6 DATA FOR SPECIMENS CURED FOR 28 DAYS AT 38º C.

CEMENT EQUIV.	IONIC CONCENTRATION mmols/l.					We	QTY OF IONS IN SOLN mmols/g			
	OH	pH	Cl	K	Na	g/g	OH	Cl	K	Na
B	427	13.63	1	388	84	0.319	136	0	124	27
C	575	13.76	1	469	107	0.313	180	0	147	33
D	646	13.81	1	495	204	0.314	203	0	155	64
E	736	13.87	1	550	198	0.311	229	0	171	62
B+NaCl	557	13.75	22	373	155	0.319	178	7	119	49
C	590	13.77	38	466	269	0.309	182	12	144	83
D	651	13.81	62	475	345	0.311	202	19	148	107
E	724	13.86	115	457	435	0.314	227	36	143	137
B+SSW	611	13.79	43	338	281	0.314	192	14	106	88
C	642	13.81	62	321	389	0.317	204	20	102	123
D	661	13.82	216	344	542	0.310	205	67	107	168
E	679	13.83	319	355	648	0.323	219	103	115	209

TABLE 7.7 DATA FOR SPECIMENS CURED FOR 56 DAYS AT 38º C.

CEMENT EQUIV.	IONIC CONCENTRATION mmols/l.					We	QTY OF IONS IN SOLN mmols/g			
	OH	pH	Cl	K	Na	g/g	OH	Cl	K	Na
B	490	13,63	2	401	88	0,285	140	1	114	25
C	588	13,77	1	526	114	0,310	182	0	163	35
D	663	13,82	2	470	197	0,300	199	1	141	59
E	747	13,87	1	560	199	0,305	228	0	171	61
B+NaCl	580	13,76	18	408	199	0,290	168	5	118	58
C	611	13,79	36	471	269	0,294	180	11	138	79
D	650	13,81	60	486	362	0,295	192	18	143	107
E	745	13,87	116	460	438	0,300	224	35	138	131
B+SSW	631	13,80	39	361	298	0,289	182	11	104	86
C	650	13,81	73	337	462	0,299	194	22	101	120
D	660	13,82	226	362	565	0,301	199	68	109	170
E	691	13,84	326	373	665	0,310	214	101	116	206

TABLE 7,8 DATA FOR SPECIMENS CURED FOR 84 DAYS AT 38º C,

CEMENT EQUIV.	IONIC CONCENTRATION mmols/l.					We	QTY OF IONS IN SOLN mmols/g			
	OH	pH	Cl	K	Na	g/g	OH	Cl	K	Na
B	513	13,71	1	422	92	0,270	139	0	114	25
C	587	13,77	1	533	102	0,302	177	0	161	31
D	675	13,83	1	490	206	0,287	194	0	141	59
E	747	13,87	1	573	200	0,291	217	0	167	58
B+NaCl	576	13,76	15	420	208	0,275	158	4	116	57
C	633	13,80	41	483	270	0,276	175	11	133	75
D	655	13,82	62	492	371	0,287	188	18	141	106
E	753	13,88	114	433	441	0,290	218	33	126	128
B+SSW	630	13,80	45	365	291	0,282	178	13	103	82
C	650	13,81	81	334	404	0,287	187	23	96	116
D	674	13,83	235	371	578	0,289	195	68	107	167
E	718	13,86	331	379	678	0,293	210	97	111	199

TABLE 7.9 DATA FOR SPECIMENS CURED FOR 168 DAYS AT 38º C.

CEMENT EQUIV.	IONIC CONCENTRATION mmols/l.					Ve	QTY OF IONS IN SOLN mmols/g			
	OH	pH	Cl	K	Na	g/g	OH	Cl	K	Na
B	525	13,72	1	432	90	0,260	137	0	112	23
C	644	13,81	2	572	108	0,275	177	1	157	30
D	690	13,84	2	515	216	0,265	183	1	136	57
E	746	13,87	1	586	208	0,272	203	0	159	57
B+NaCl	575	13,76	20	457	208	0,250	144	5	114	52
C	659	13,82	42	483	294	0,252	166	11	122	74
D	651	13,81	61	448	385	0,275	179	17	123	106
E	746	13,87	113	438	457	0,273	204	31	120	125
B+SSW	636	13,80	36	371	299	0,272	173	10	101	81
C	657	13,82	69	337	413	0,280	184	19	94	116
D	697	13,84	245	384	591	0,278	194	68	107	164
E	719	13,86	350	390	684	0,280	201	98	109	192

TABLE 7.10 DATA FOR SPECIMENS CURED FOR 504 DAYS AT 38º C.

CEMENT EQUIV.	IONIC CONCENTRATION mmols/l.					We	QTY OF IONS IN SOLN mmols/g			
	OH	pH	Cl	K	Na	g/g	OH	Cl	K	Na
B	536	13,73	2	455	105	0,247	132	0	112	26
C	652	13,81	2	593	114	0,250	163	0	148	29
D	695	13,84	2	534	220	0,247	172	0	132	54
E	760	13,88	2	597	205	0,255	194	0	152	52
B+NaCl	623	13,79	16	474	214	0,240	150	4	114	51
C	679	13,83	41	493	302	0,241	164	10	119	73
D	662	13,82	75	463	400	0,260	172	20	120	104
E	772	13,89	127	448	468	0,265	205	34	119	124
B+SSW	649	13,81	34	377	310	0,260	169	9	98	81
C	666	13,82	50	349	426	0,265	176	13	92	113
D	709	13,85	263	403	625	0,259	184	68	104	162
E	741	13,87	373	411	723	0,263	195	98	108	190

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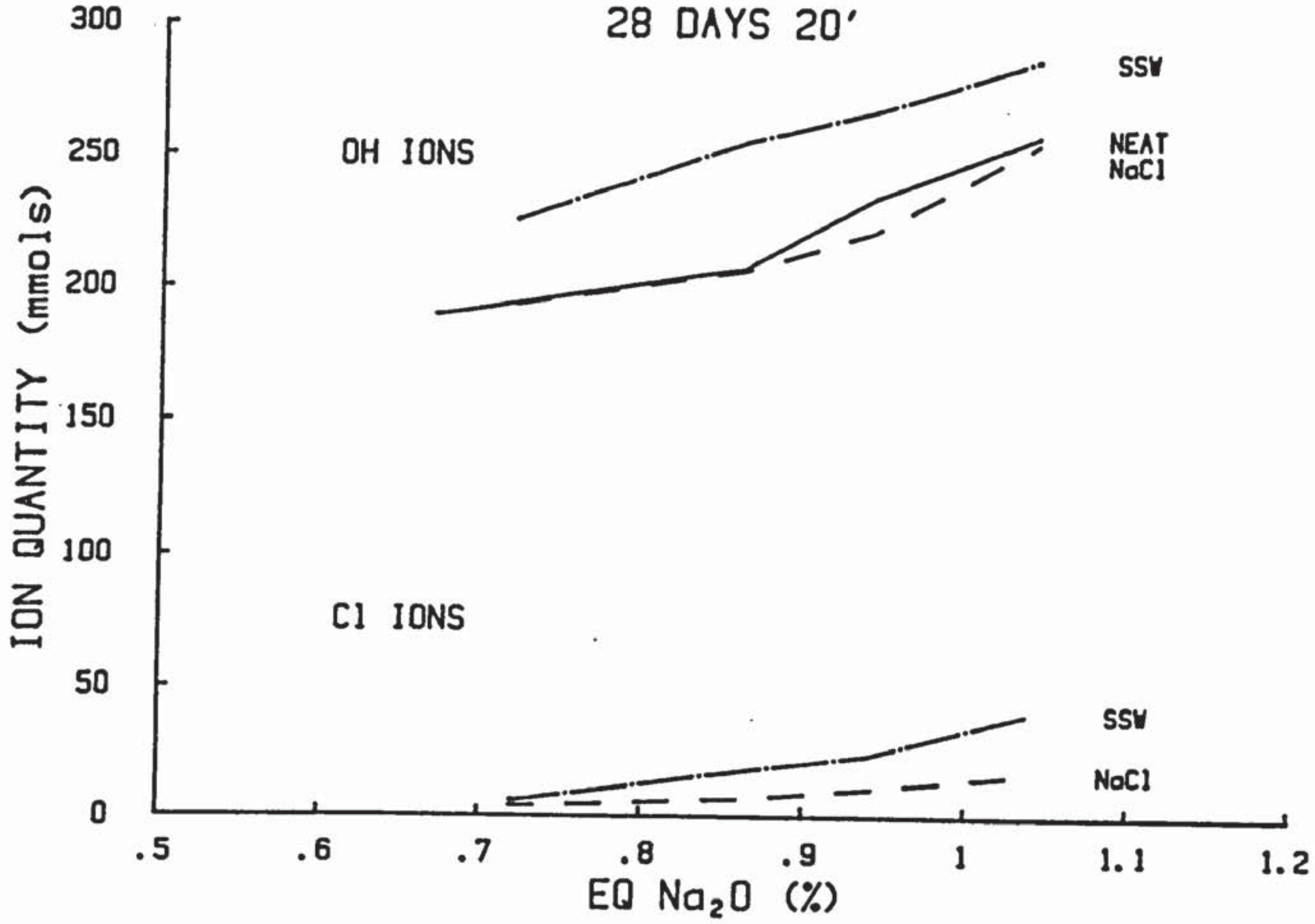
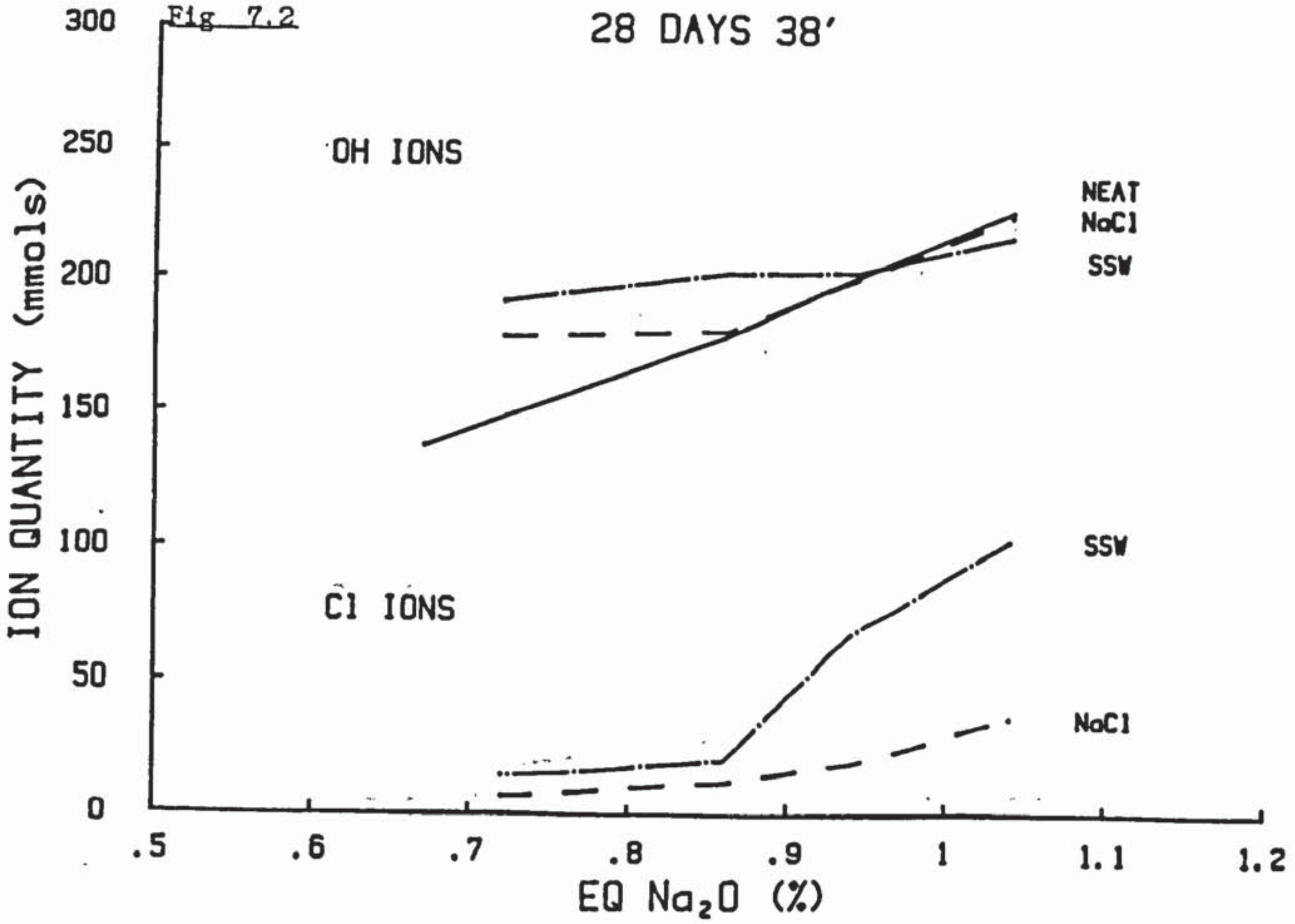


Fig 7.1

The influence of alkali salts on the quantity of anions in solution

Fig 7.2



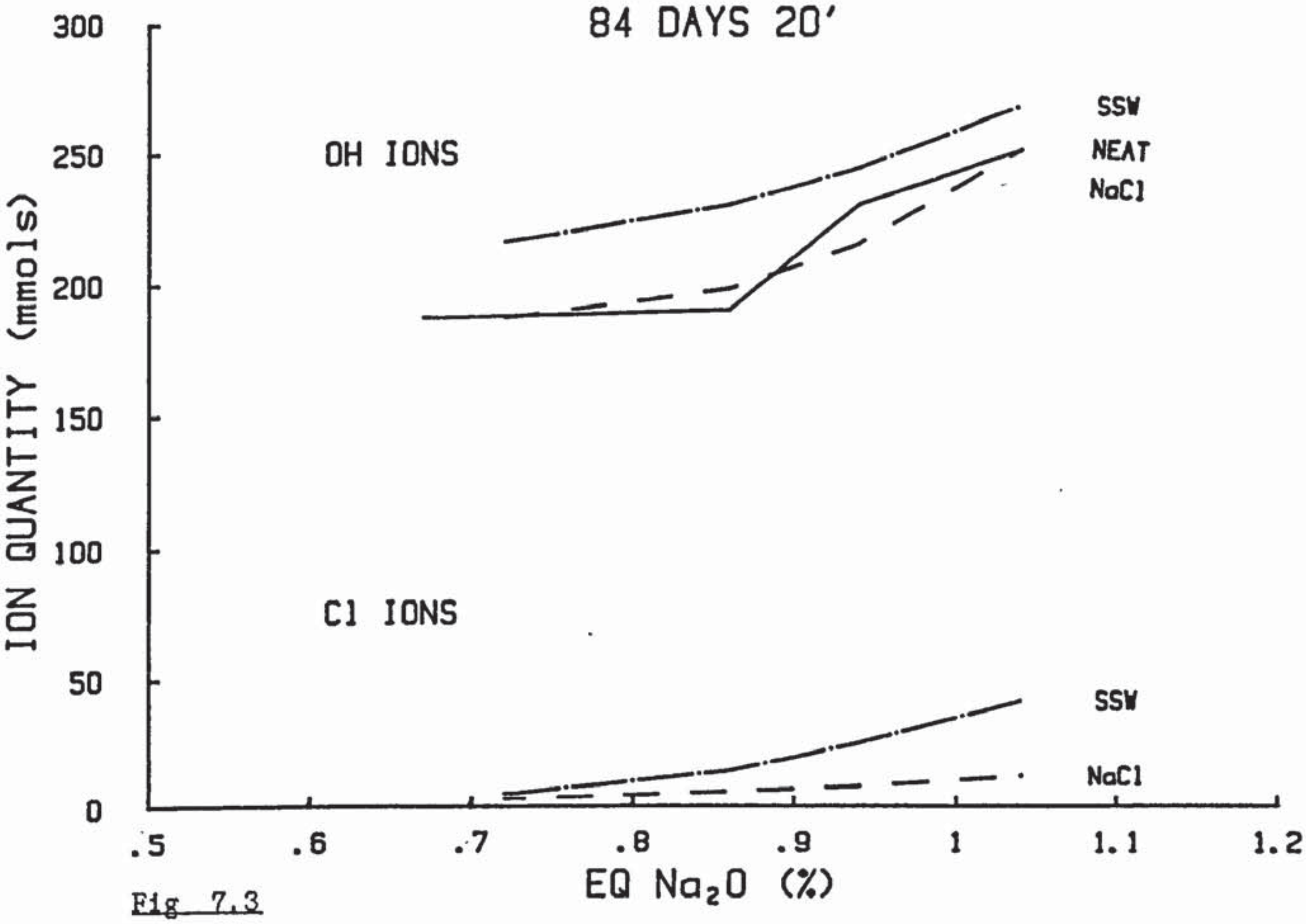
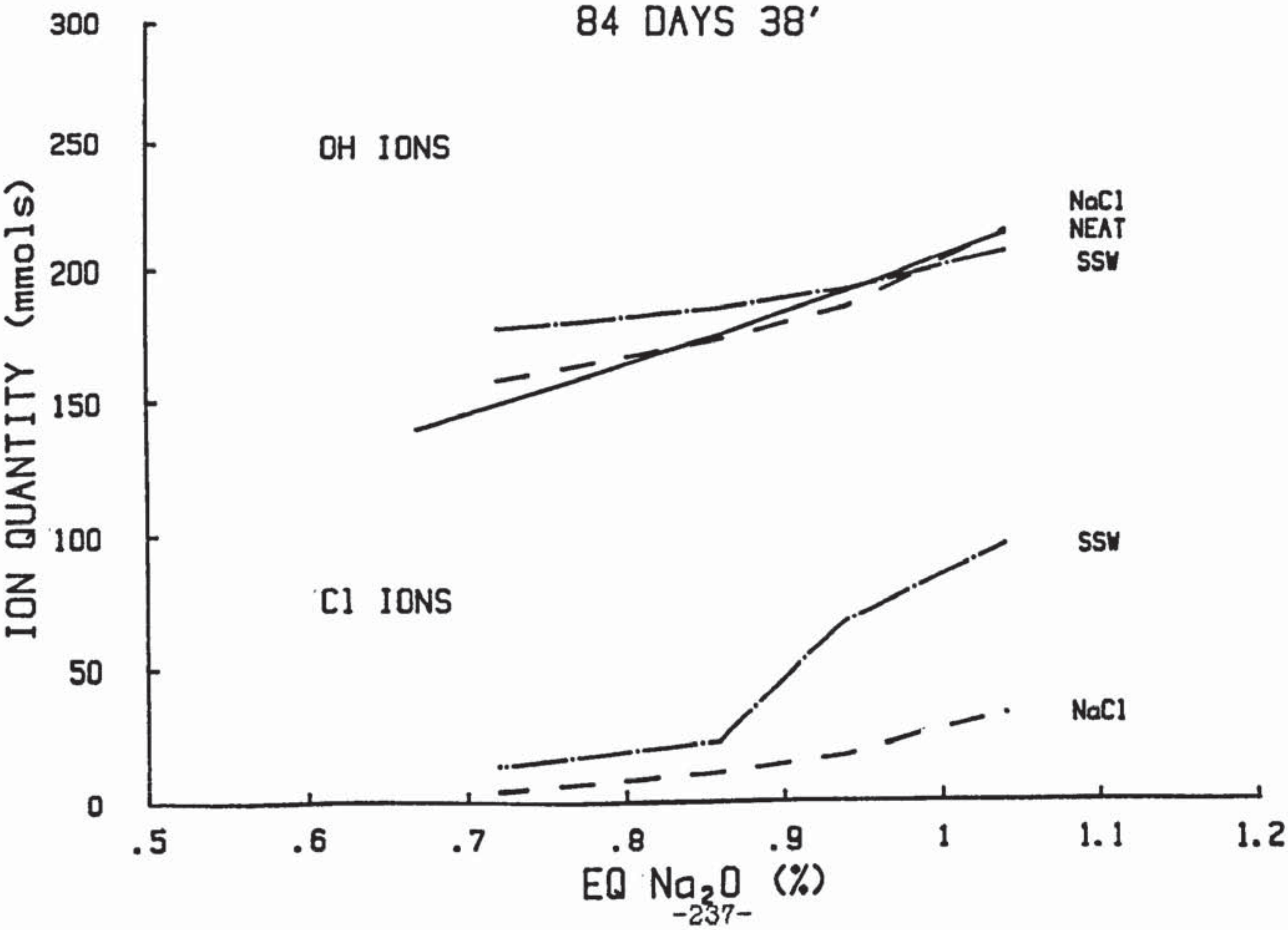


Fig 7.3

The influence of alkali salts of the quantity of anions in solution

Fig 7.4



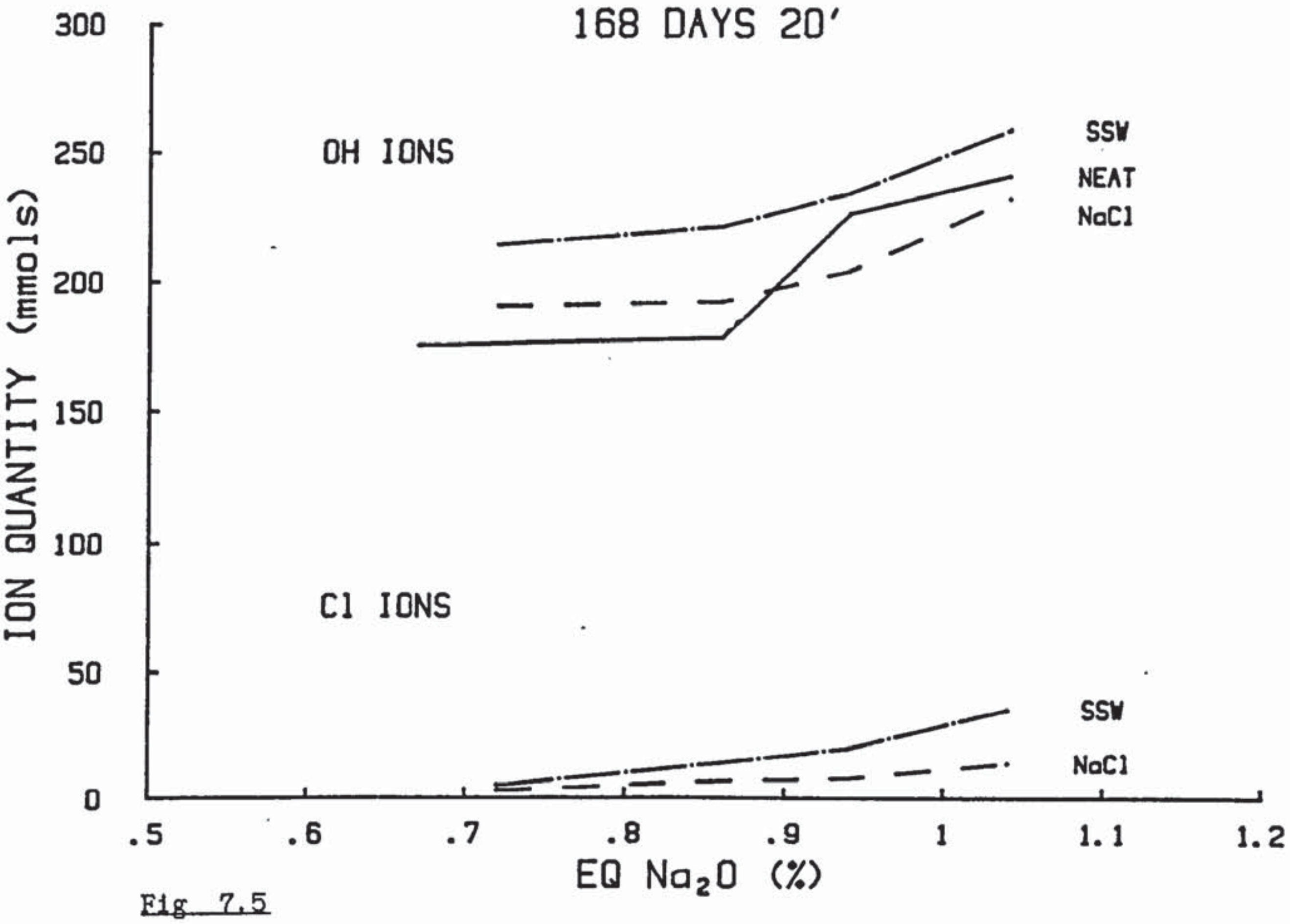
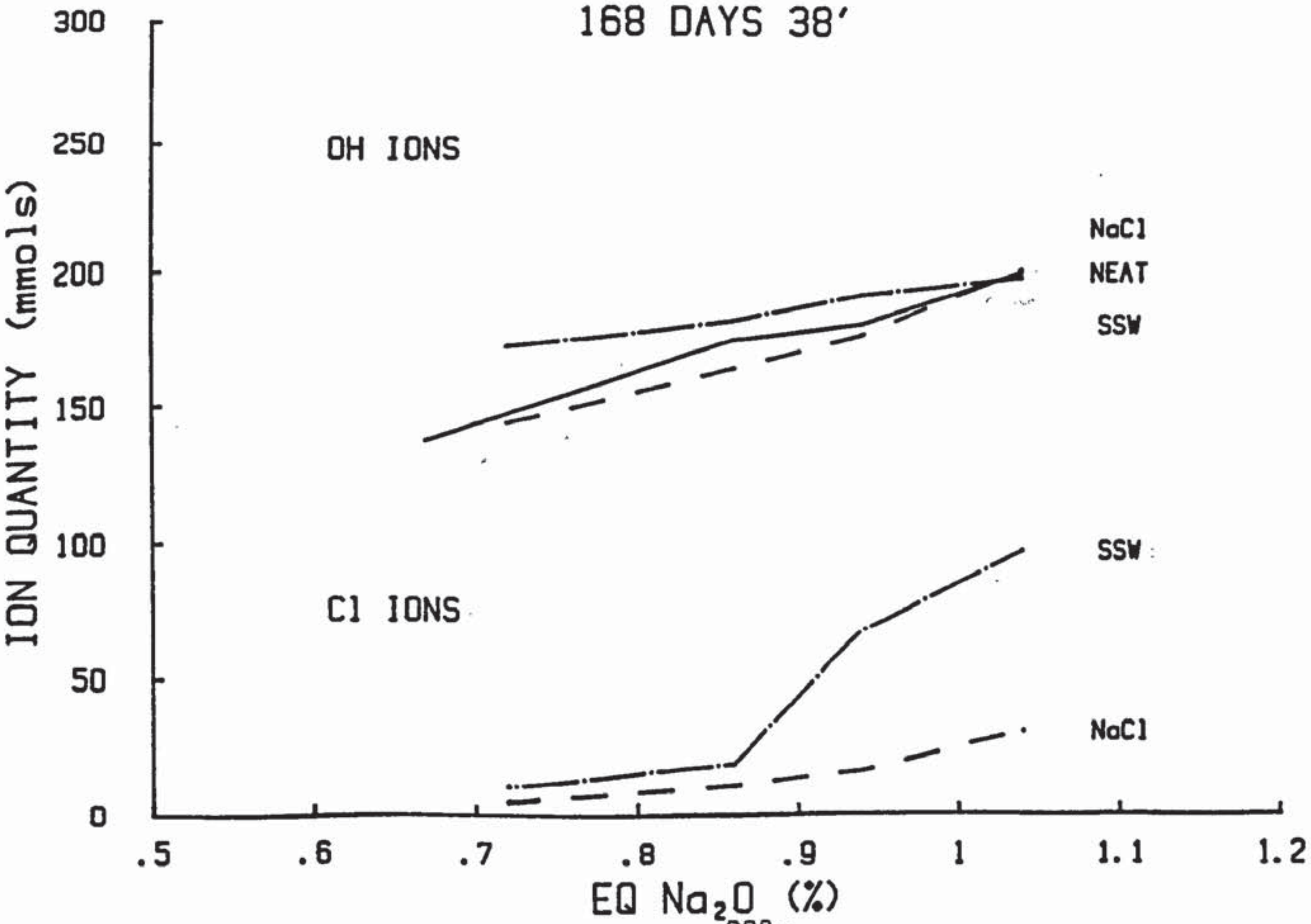


Fig 7.5

The influence of alkali salts on the quantity of anions in solution

Fig 7.6



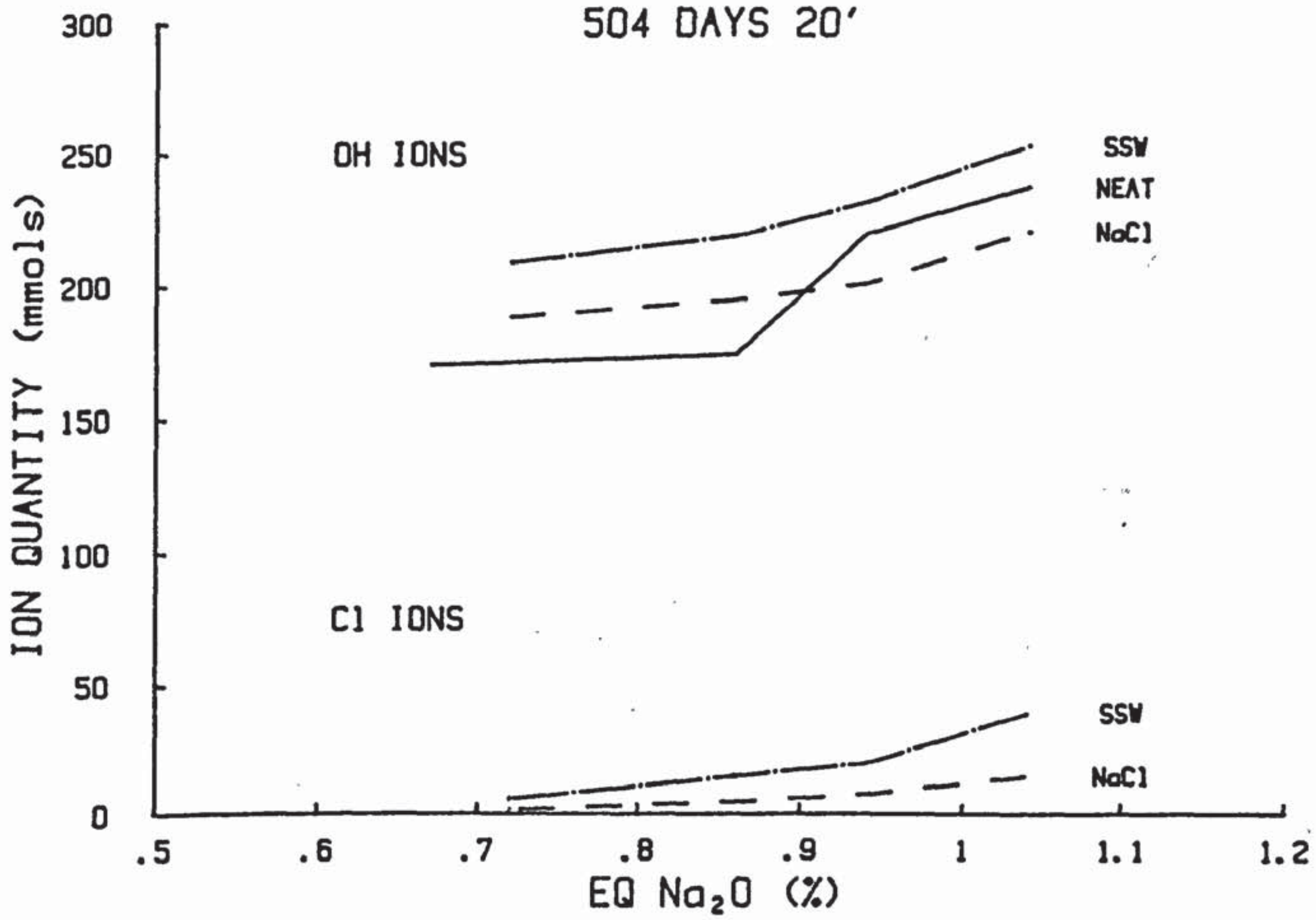
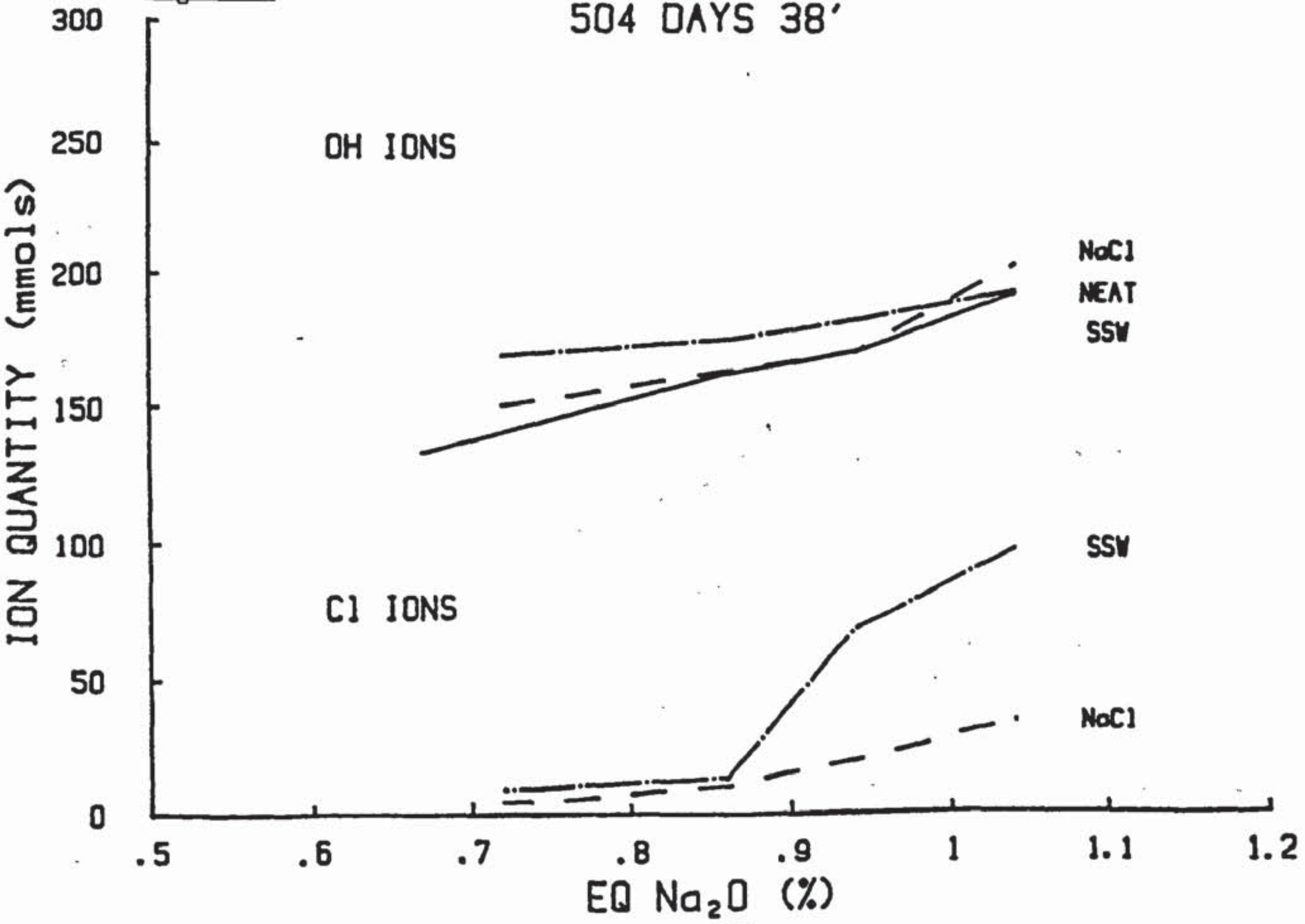


Fig 7.7

The influence of alkali salts on the quantity of anions in solution

Fig 7.8



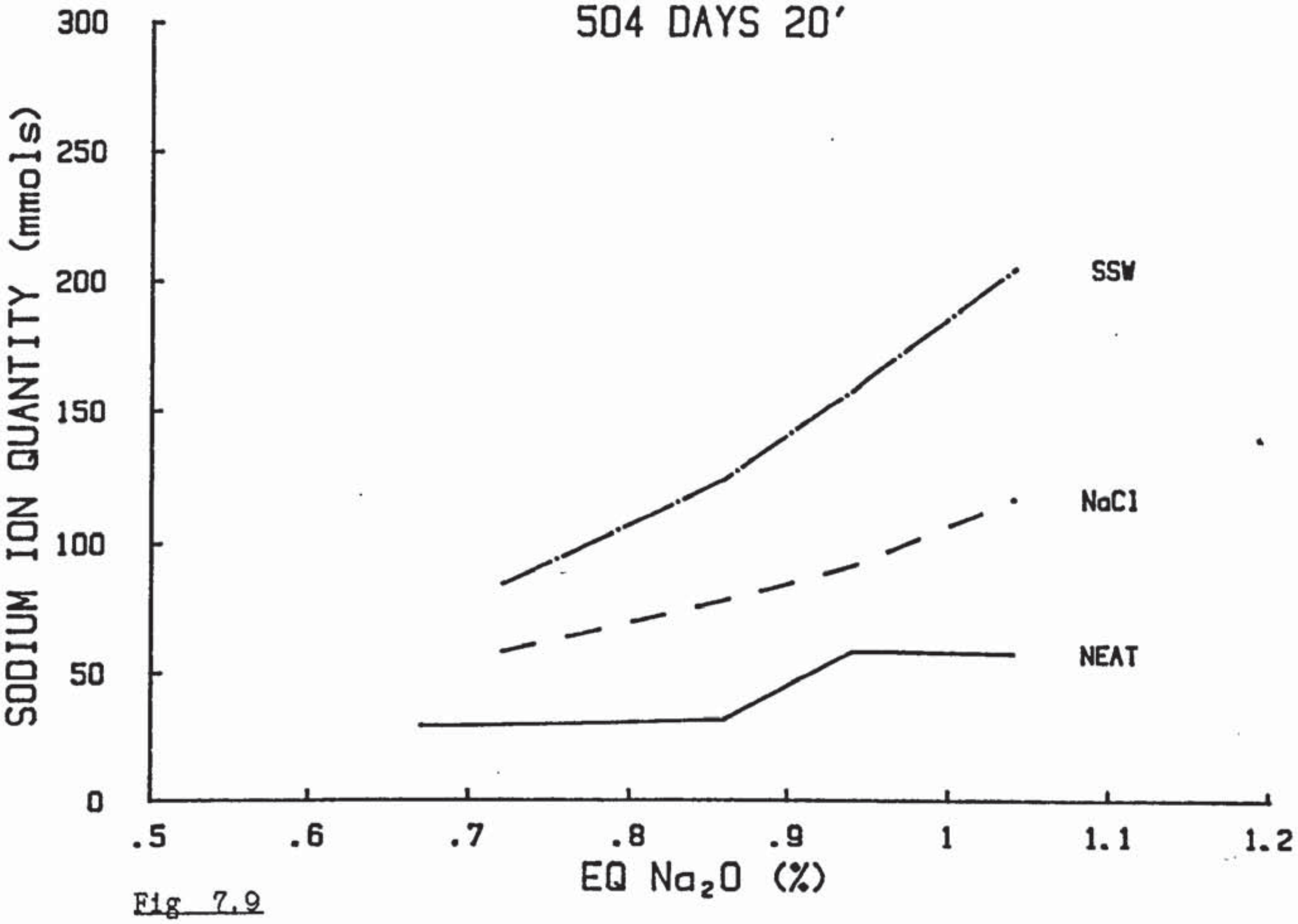
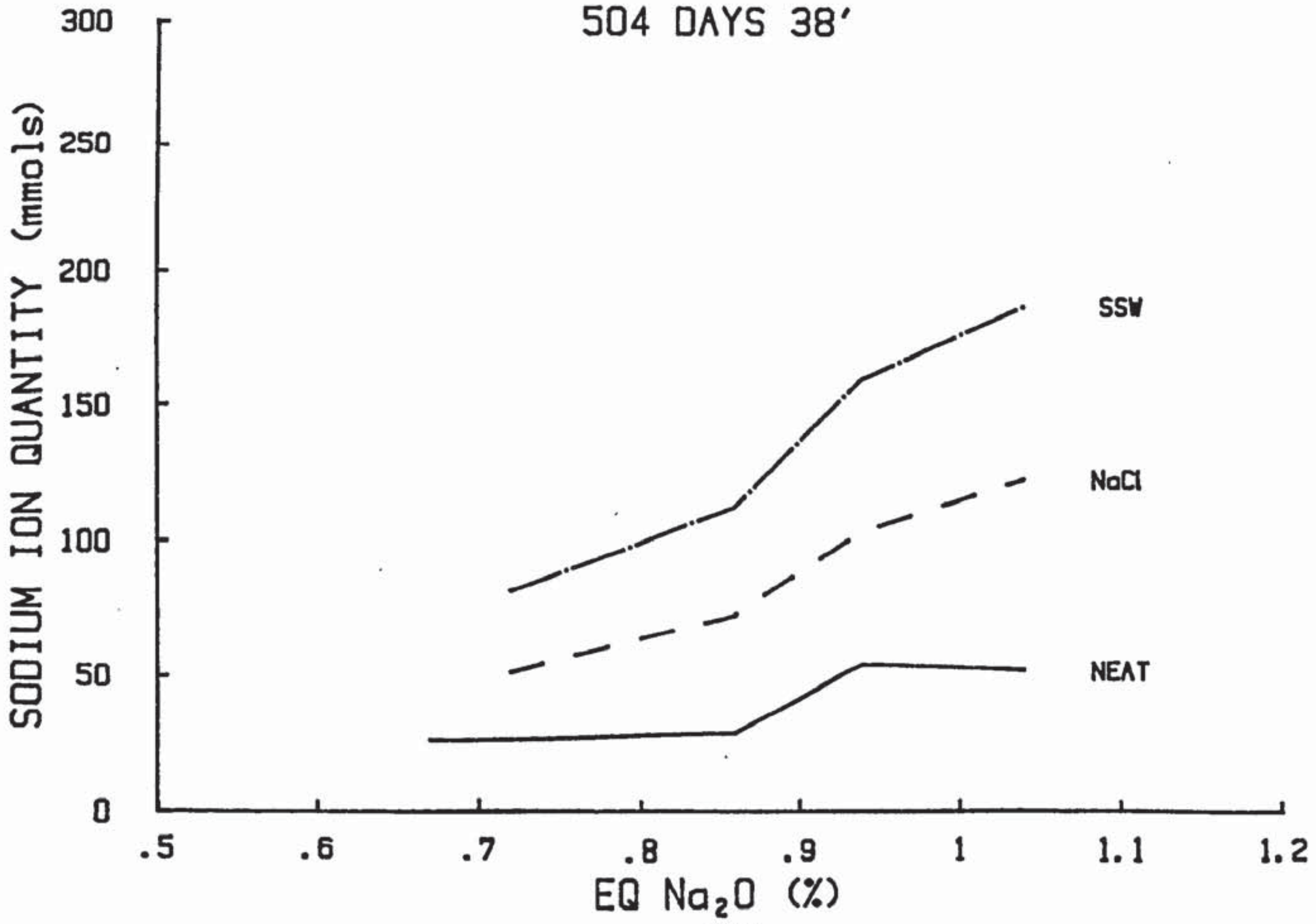


Fig 7.9

The influence of alkali salts on the quantity of sodium ions in solution

Fig 7.10



APPENDIX 8

Published work from the study

Magazine of Concrete Research: Vol 38, No 134: March 1986

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SODIUM CHLORIDE AND ALKALI AGGREGATE REACTION

by P J Nixon*, C L Page+, I Canham+ and R Bollinghaus*

SUMMARY

Sodium chloride is a common contaminant of sands and gravels, especially those dredged from the sea. The possibility that it may enhance the alkalinity of concrete and hence may exacerbate alkali aggregate reactions is therefore a matter of importance. This paper describes the results of experiments in which the effect of sodium chloride and synthetic sea water added at the mixing stage on both the composition of the pore solution in cement pastes and the expansion of mortars and concretes containing reactive aggregates has been explored.

It was found that both sodium chloride and synthetic sea water elevated the hydroxyl ion concentration of the cement pastes to a level similar to that produced by a Portland cement with an equivalent alkali level. Similarly the sodium chloride and synthetic sea water had an effect on the expansion of mortars and concretes which was in line with the effect produced by an equivalent amount of alkali in the cement.

Footnote: * Building Research Establishment UK
+ Aston University UK

INTRODUCTION

Sodium chloride is a common contaminant of sands and gravels, especially those dredged from the sea. It is also extensively used as a deicing salt on roads. The possibility that it may enhance the alkalinity of concrete and hence may exacerbate alkali aggregate reactions is therefore a matter of importance. This paper describes the results of experiments in which the effect of sodium chloride and synthetic sea water added at the mixing stage on both the composition of the pore solution in cement pastes and the expansion of mortars and concretes containing reactive aggregates has been explored.

PORE SOLUTION COMPOSITION

The composition of the pore solution expressed from three series of pastes was determined. Each series consisted of cement paste specimens with 0.47 water/cement ratio which were cured in sealed containers for increasing periods from 28 to 504 days. For each series two sets of specimens were made, one set cured at 20°C the other at 38°C. The first series was made with four Portland cements (A, B, C, D) with alkali contents of 0.67, 0.86, 0.94 and 1.06% sodium oxide equivalent respectively. The second series consisted of specimens made using cement A as base but with additions of sodium chloride, via the mixing water, such that the total calculated sodium oxide equivalent was the same as the cements in the first series together with an additional mix with 0.775% Na_2O equivalent. In the third series synthetic sea water powder (BDH to meet DEF 1053, BS 3900) was used and again additions were made to cement A in order to produce alkali levels equivalent to the Portland cements A to D plus the additional mix.

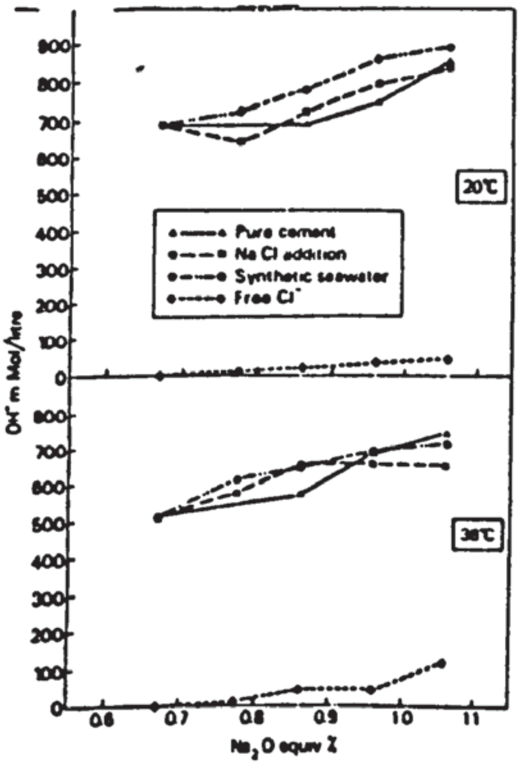

Figure 1 Effect of chloride additions on hydroxyl ion concentrations 84 days storage. w/c = 0.47

After demoulding the specimens were pressed as previously described by Page and Vennesland (1983). The expressed fluid was collected in a plastic syringe and analysed for OH^-, Na^+, and Cl^-. At each age the proportions of evaporable and non-evaporable water in the specimens were estimated by heating to constant weight at 105°C. (The effect of the addition of sodium chloride and synthetic sea water on the hydroxyl ion concentration of pastes stored for 84 days is shown in Figure 1 compared with the effect of an equivalent rise in the alkali level of the Portland cement). The free chloride ion produced by the sodium chloride addition is also shown.

EXPANSION OF MORTAR PRISMS

The length change of mortar prisms (275 x 25 x 25 mm) made with the same series of cements and additions of sodium chloride or synthetic sea water was monitored. The reactive aggregate was Beltane opal, a porous opaline rock from the Beltane quarry, California. It was used in the 150 to 300 micron fraction in a proportion of 12 g per 100g cement, which is a proportion close to that found to give the maximum expansion at this level of alkali. The remaining aggregate was a crushed Carboniferous limestone. The water/cement was 0.47 and the aggregate/cement was 2.75.

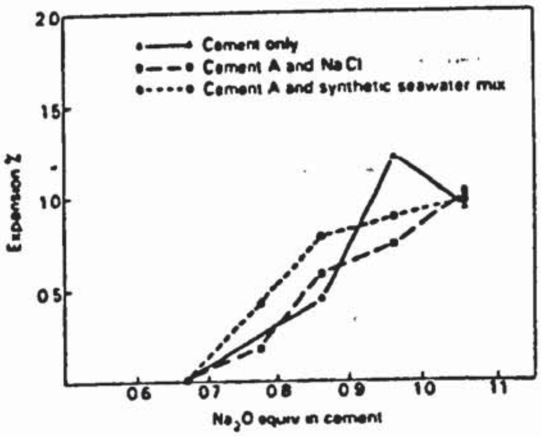

Figure 2 Expansion at 1 year of mortar prisms made with Beltane opal.
Storage temperature 38°C

The prisms were stored in a water saturated atmosphere either at 20 or 38°C. The expansions at 1 year of mortars stored at 38°C are shown in Figure 2.

EXPANSION OF CONCRETE PRISMS

Tests have also been carried out in which the length change of concrete prisms containing a reactive flint sand have been monitored. This sand contains about 40% flint concentrated in the 1.18 to 5 mm fractions. It was used as 30% of the whole aggregate, with carboniferous limestone coarse aggregate so the flint content of the whole aggregate was about 12%. Examination of concrete from structures in the UK affected by alkali aggregate reaction and containing similar aggregate combinations together with laboratory studies (Nixon and Bollinghaus, 1983) have shown this to be a reactive proportion. However, to demonstrate alkali reactivity under laboratory conditions with UK aggregates even those of a type known to have been used in concrete structures affected by alkali aggregate reaction it has been found necessary to subject the aggregates to highly alkaline conditions. The threshold of reactivity for this particular aggregate in laboratory tests has been found to be about 5.6 kg of sodium oxide equivalent per cubic metre of concrete.

In these tests the concrete was made with 400 kg/m³ of the high alkali cement C such that the alkali level in the concrete was 3.84 kg Na_2O equivalent/m³. The water/cement ratio was 0.45. A series of mixes was made with the concrete in which sodium chloride was added in the mixing water to give calculated Na_2O equivalent levels of 5, 6 and 7 kg/m³.

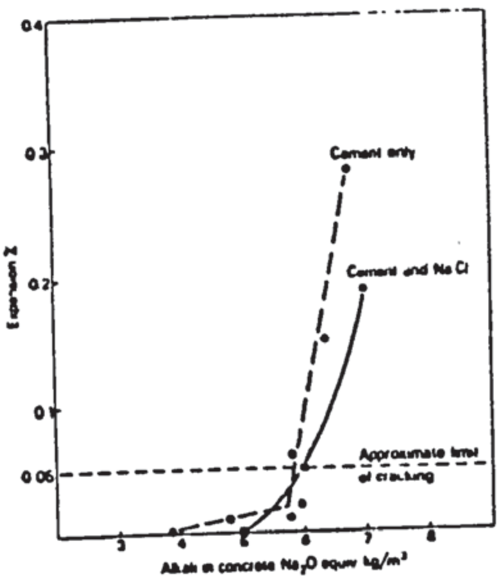

Figure 3 Expansion at 1 year of concrete prisms containing 30% flint sand and stored at 38°C and 100% RH

The prisms were stored at 100% RH and 38°C after demoulding at 1 day and length change on duplicate prisms was monitored up to 1 year. The mean results of the expansion measurements are compared in Figure 3 with those in which the enhanced alkalinity was obtained by increasing the cement content.

DISCUSSION

The analyses of the expressed pore solutions show that the hydroxyl ion concentration in solution rose in line with the alkali content of the Portland cement, albeit rather erratically in some cases. Some of this erratic behaviour may reflect differences in the proportions of the total alkali present as the readily soluble sulphate compared with that in solid solution in the cement minerals. The hydroxyl ion concentrations in the pastes to which sodium chloride or synthetic sea water was added, also increased in line with the calculated alkali level in the paste and in a roughly equivalent manner to the series of control Portland cements.

The synthetic sea water mix consistently produced more hydroxyl ions than the sodium chloride or the equivalent cement. This is understandable as in addition to sodium chloride sea water contains small amounts of potassium and sulphate ions which will also contribute to the hydroxyl ion concentration. The free chloride ion concentration increases in the pastes with higher levels of chloride addition. This increase is more noticeable at 38°C than 20°C. It suggests that the complexing ability of the aluminate phases in this cement (which has a C_3A content of 11.7%) is being exhausted. This is also shown by the tailing-off in the rate of increase of hydroxyl ion concentration at the higher alkali levels at 38°C. The sharp increase in free chloride ion corresponds to an addition of 0.3% chloride ion by weight of cement. This suggests that in concrete likely to be subjected to elevated temperatures for long periods the current BS 8110 limit of 0.4% chloride ion by weight of cement in reinforced concrete may be a little high.

The good correlation between the behaviour of cement pastes containing added chloride and the control series of different Portland cements was also found in the experiments with mortar bars containing beltane opal.

The concrete prisms containing flint sand and added sodium chloride started to show deleterious expansions at very similar levels of alkali to prisms in which the alkalinity was produced by the cement only. At higher alkali levels the expansions of the chloride-containing prisms were lower. This is to be expected, as to produce an alkali level in the concrete of 6 kg/m^3 the addition level of chloride ion was 0.62% by weight of cement and to produce 7 kg/m^3 the chloride added was 0.90%. At these levels there would be appreciable free chloride and hence lower hydroxyl ions levels.

Overall then there is clear evidence that addition of sodium chloride or synthetic sea water to a cement paste, mortar or concrete at the mixing stage can result in both an elevation of the hydroxyl ion concentration in the pore solution and an exacerbation of the alkali aggregate reaction. In the UK this is being taken into account in the recommendations for minimizing the risk of damage from alkali silica reaction (The Concrete Society 1986). One of the principal recommended ways of minimizing the risk of damage from alkali silica reaction is by limiting the total alkali level originating from the cement in each cubic metre of concrete mix to no more than 3 kg of sodium oxide equivalent. However, where alkalis are contributed to the concrete from sources other than the cement it is recommended that the limit is reduced by an appropriate amount. If the source of alkali is sea salt contamination of aggregates the equivalent alkali should be calculated from:-

$$E = \frac{0.76}{100} \times (CF \times MF + CC \times MC)$$

where E = alkali contribution made to the concrete by the salt (kg/m^3 of Na_2O equivalent)

CF & CC = chloride ion content of the fine and coarse aggregates respectively as a percentage by mass of dry aggregate measured according to BS 812.

MF & MC = fine and coarse aggregate content of the concrete (kg/m^3).

The factor of 0.76 has been derived emperically from the chemical analyses of typical samples of sea water.

CONCLUSIONS

Introduction of sodium chloride or synthetic sea water to a cement paste, mortar or concrete at the mixing stage results in an elevation of the hydroxyl ion concentration of the pore solution to a level similar to that produced by a Portland cement with an equivalent alkali level. This in turn can increase the likelihood and severity of damage from alkali aggregate reaction, if the mortar or concrete contains a reactive aggregate, to an extent in line with the effect produced by an equivalent amount of alkali in the cement. If the alkali content of the concrete is being controlled in order to avoid damage from alkali aggregate reaction the alkali contributed by salt contamination of the aggregate or other source of sodium chloride should be taken into account.

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ASPECTS OF THE PORE SOLUTION CHEMISTRY OF BLENDED CEMENTS RELATED TO THE CONTROL OF ALKALI SILICA REACTION

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ABSTRACT

The effects of four pulverised fuel ashes (PFA) and three ground blastfurnace slags (GBFS) on the alkalinity of the pore solution phase of hardened cement pastes has been studied. It has been found that the total alkali content of a PFA is an important factor, but not the only one, determining its effectiveness in reducing the hydroxyl ion concentration of the pore solution. For GBFS, however, there was found to be no direct correlation between the total alkali content of the slag and the composition of the pore solution. Implications regarding the roles of PFA and GBFS in reducing expansion associated with alkali silica reaction (ASR) are discussed.

Introduction

Interest in the use of PFA and GBFS to control ASR in concrete has led to a number of recent investigations into the effects of these materials on the pore solution alkalinity of the cement matrix (1-6) and on relationships between their composition and relative ability to suppress expansion in the presence of reactive aggregates (2,5,7,8,9). Both GBFS and PFA contain considerable quantities of total alkalis, the levels in typical slags being comparable to those in Portland cements of high alkali content whilst those in PFA may be as high as 4.6% equivalent Na_2O (10). These alkalis are initially bound within the glassy matrix of the slag or ash and it is clearly important to elucidate the balance between their release as the glass reacts with the cement pore liquid and their incorporation into hydration products.

This paper presents further evidence of the influence of the total alkali level of a number of PFA's and GBFS's on the hydroxyl ion concentration of the pore solution phase associated with cement pastes in which they were blended with a Portland cement of medium alkali content. The materials selected for study represented a wide range of total alkali contents. In the case of the PFA's, there were also significant variations in fineness and pozzolanicity between the different ashes whilst, in the case of the GBFS's, effects of different methods of manufacture were represented.

Experimental

Blended cements were produced by partial replacement of a Portland cement of equivalent Na_2O content, 0.67 %, with a series of four PFA's and three GBFS's. In the case of the PFA's, the proportions by weight of cement replaced were 20 % and 40 %, whilst for the GBFS's, they were 40 % and 60 %. The chemical compositions of all the materials used are presented in Table 1 and a summary of the physical properties of the PFA's is given in Table 2.

TABLE 1
Chemical Compositions of Materials

% Weight	Cement	PFA1	PFA2	PFA3	PFA4	GBFS1	GBFS2	GBFS3
CaO	63.3	1.4	1.7	2.7	2.7	39.4	36.5	42.3
SiO_2	19.5	51.1	51.2	49.3	48.1	36.7	40.0	36.0
Al_2O_3	6.4	25.8	24.5	33.5	31.2	11.5	7.5	9.4
Fe_2O_3	3.1	8.8	9.1	5.5	5.6	0.7	2.0	0.9
SO_3	2.8	0.7	0.6	0.4	0.3	1.3	0.2	0.9
MgO	2.1	1.4	1.4	1.3	1.3	7.8	9.8	7.4
TiO_2	-	1.0	0.9	1.3	1.2	0.6	0.4	0.6
K_2O	0.84	3.05	2.97	1.16	1.10	0.82	0.58	0.47
Na_2O	0.12	1.36	1.25	0.28	0.25	0.43	0.36	0.29
L.O.I.	4.2	4.2	4.9	2.0	6.8	-	-	0 -
Eq. Na_2O	0.67	3.37	3.20	1.04	0.97	0.97	0.74	0.60

Note: GBFS1 and GBFS3 were granulated slags. GBFS2 was a pelletized slag.

TABLE 2
Summary of Properties of Pulverised Fuel Ashes

	PFA1	PFA2	PFA3	PFA4
Description	High Alkali Fine Ash	High Alkali Coarse Ash	Low Alkali Fine Ash	Low Alkali Coarse Ash
Eq Na_2O (%)	3.37	3.20	1.04	0.97
45μm Residue (12.5% max)	4.4	13.8*	4.6	16.4*
MgO (4% max)	1.4	1.4	1.3	1.3
SO_3 (2.5% max)	0.7	0.6	0.4	0.3
L.O.I. (7% max)	4.2	4.9	2.0	6.9
Water Req (95% max)	89	89	87	96*
Pozzolanic Index (89% min)	131	103	112	90
Pozzolanicity Rating	1	2	2	4

* Failure to comply with BS 3892:Part 1

Pastes of water/solids ratio 0.45 were prepared from each of the blended cements and from the unblended Portland cement. These were cast into plastic cylinders and stored under sealed conditions at 20 °C for periods of 28, 84, 168 and 365 days.

Pore solutions were expressed from the hydrated specimens by means of a device similar to those described by previous investigators (11,12). The hydroxyl ion concentrations of the solutions were determined by titration with nitric acid in the presence of phenolphthalein.

Results and Discussion

The concentrations of hydroxyl ion in the pore solutions of the various materials are shown as functions of curing time in Figs. 1 - 4. Points on the graphs represent the averages of duplicate measurements and the designations 1,2 etc. refer to PFA1, PFA2 (or GBFS1, GBFS2) etc. The line denoted C refers to data obtained for the unblended cement, whilst that labelled C' represents the concentrations expected if the PFA or GBFS is assumed to behave simply as a 'cement of zero alkali content', which contributes no alkalis to the pore solution but binds water in the same proportion as does Portland cement.

Effects of PFA

The results presented in Figs. 1 and 2 confirm a number of trends reported in previous investigations. Thus, for all the PFA's studied, the hydroxyl ion concentrations of the pore solutions were found to decrease both with increasing time and with increasing level of cement substitution. At times of 84 days or longer, the reductions in alkalinity were all significantly greater than those corresponding to lines C' (as defined above). These observations are consistent with those of an earlier study by Nixon et al (4) in which the pore solution compositions of pastes containing a single PFA of high alkali content (0.96% Na_2O, 3.71% K_2O) and cements of equivalent Na_2O contents 0.94%, 0.86%, 0.67% and 0.23% were measured for times ranging from 28 to 365 days; except in the case of the lowest alkali cement studied in (4), substitution of cement with PFA reduced the hydroxyl ion concentration of the pore liquid similarly to the effects shown in Figs. 1 and 2.

The importance of the alkali content of PFA's as a determinant of their effectiveness in reducing the hydroxyl ion concentrations of pore solutions is clearly demonstrated by comparing the data for ashes 1 and 2 with those for ashes 3 and 4 (see Figs. 1 and 2). This shows the materials of lower alkali contents to be significantly the more effective and confirms the observations of Kollek et al (5) who examined the influence of two PFA's of equivalent Na_2O contents, 0.97% and 3.17%, in mortars hydrated for 180 days.

Aside from alkali content, other characteristics of the PFA's studied appear to have had only a modest influence on their effectiveness in reducing hydroxyl ion concentrations. Comparing the two ashes of lower alkali content, however, the results shown in Figs. 1 and 2 suggest that the more reactive pozzolana (PFA 3) was somewhat more effective than its coarser, less reactive counterpart (PFA4).

Effects of GBFS

The results shown in Figs. 3 and 4 indicate that all three of the slags, when used as replacements for 40% or 60% Portland cement, produced pastes with hydroxyl ion concentrations lower than those of the unblended cement paste. The abilities of the various slags to reduce the alkalinity of the pore solution varied considerably, however, and only in the case of GBFS2, a pelletised slag of medium alkali content and high reactivity (as indicated by strength development), were the observed reductions in hydroxyl ion concentration greater than those corresponding to the lines C' (as defined above). Similarly wide variations in the effectiveness of different slags in terms of alkali reduction have been noted by other researchers (3,5,6,13).

On the basis of the present results and those reported elsewhere, there does not appear to be a good correlation between the total alkali content of a slag and its ability to reduce hydroxyl ion concentrations in blended cement pastes. Other factors related to the reactivity of the slag, its glass content and C/S ratio may be more important as these would be expected to affect the quantity and composition of CSH formed, silica-rich CSH gels having enhanced tendencies to remove alkalis from solution (3). Although results of the present investigation support such an argument, the position remains unclear as other workers have not found a correlation between slag reactivity and ability to remove hydroxyl ions (5).

In general GBFS's do not seem to be particularly efficient as alkali removers when compared with other cement extenders that are used to control ASR, such as PFA or microsilica(14,15). It would also appear from the results shown in Figs. 3 and 4 that, in contrast with the behaviour recorded for specimens containing PFA, there is little tendency in pastes containing GBFS for progressive reduction in hydroxyl concentration to take place after the first 28 days of hydration. The ability of slag cements to suppress ASR in practice therefore suggests that some additional mechanism, besides alkalinity reduction, may also be involved. This suggestion has previously been made by Bakker who argues that beneficial effects of slag cements in relation to ASR are mainly due to the fact that their ability to restrict transport of water and ionic species to reaction sites is much higher than that of typical unblended cement pastes (16).

A final point with regard to the influence of PFA and GBFS on pore solution composition is that the proportion of chemically bound water in mature hydrated cement pastes of constant water/solids ratio tends to decrease as the proportion of cement replacement is increased.This implies that part of the effect of PFA or GBFS on the hydroxyl ion concentration of the pore solution phase is simply ascribable to dilution as a function of the quantity of residual free water. If it is assumed that the relative volumes of free water within the various pastes are reflected approximately in their relative

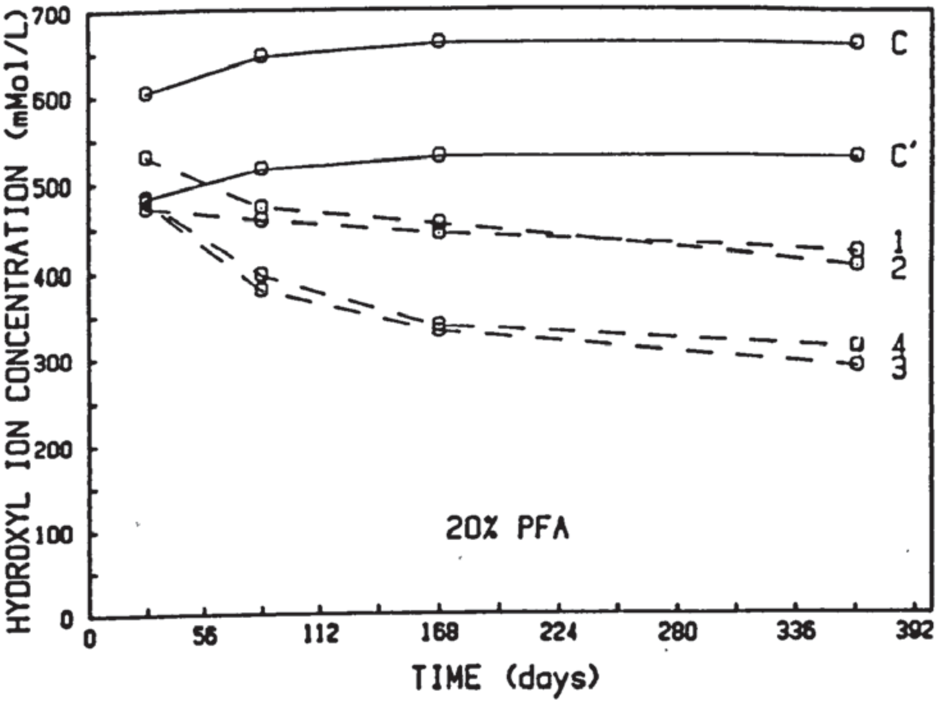

FIG. 1
Hydroxyl ion concentrations in pore solutions of Portland cement paste (C) and blended pastes containing 20% various PFA's (1,2,3,4) or 20% hypothetical cement of zero alkali content (C').

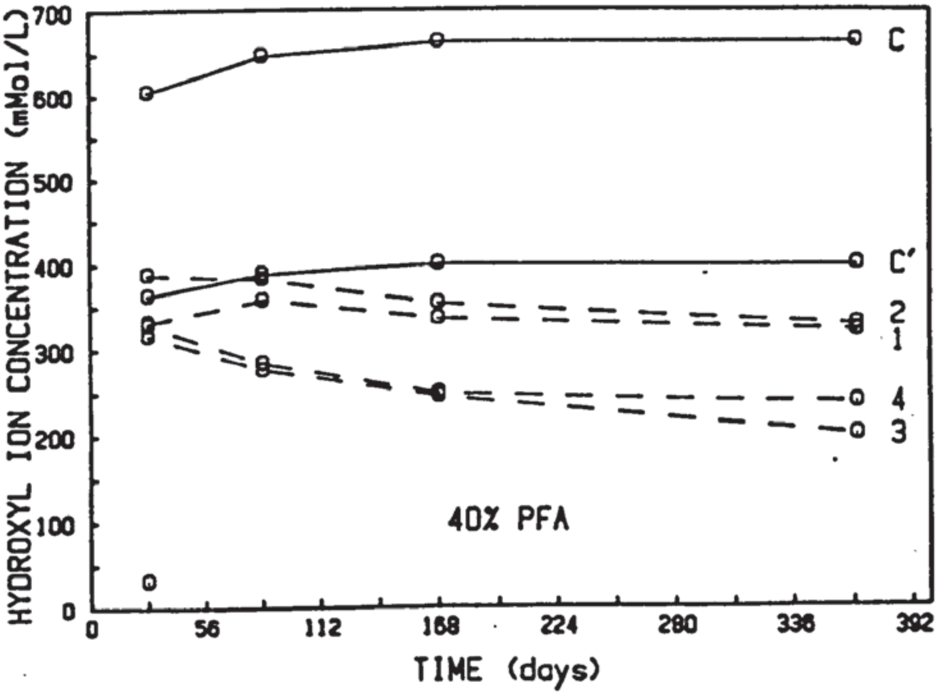

FIG. 2
Hydroxyl ion concentrations in pore solutions of Portland cement paste (C) and blended pastes containing 40% various PFA's (1,2,3,4) or 40% hypothetical cement of zero alkali content (C').

evaporable water contents, the total quantities of dissolved hydroxyl ion in the pore solutions are such that the PFA's and GBFS's studied appear slightly less effective as reducers of soluble alkalis than would be indicated from the concentrations plotted in Figs, 1-4. As has been discussed recently elsewhere in relation to PFA (17,18), however, this effect is not a large one and the general conclusions that have been reached on the basis of comparing concentrations remain substantially unaltered even when changes in the free water contents of the material are taken into account.

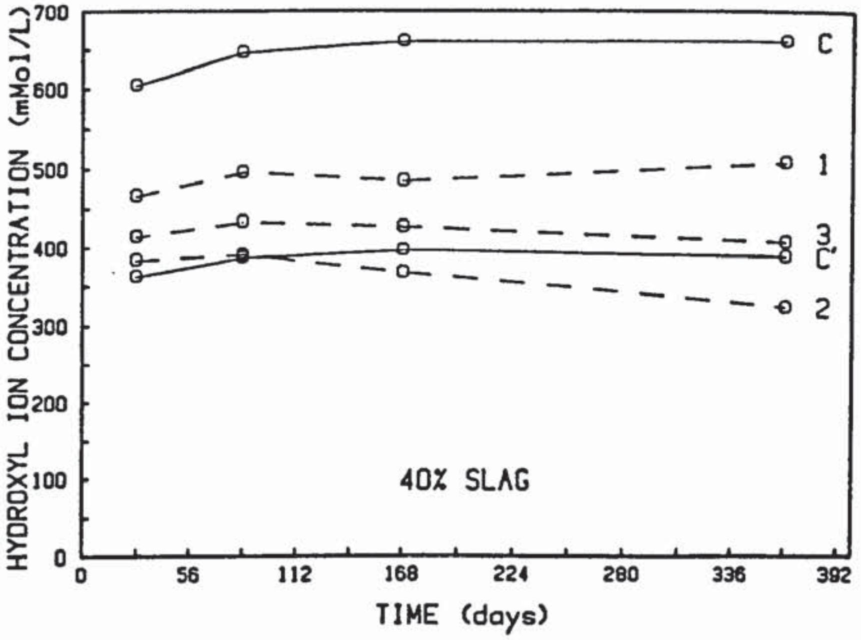

FIG. 3
Hydroxyl ion concentrations in pore solutions of Portland cement paste (C) and blended pastes containing 40% various GBFS's (1,2,3) or 40% hypothetical cement of zero alkali content (C').

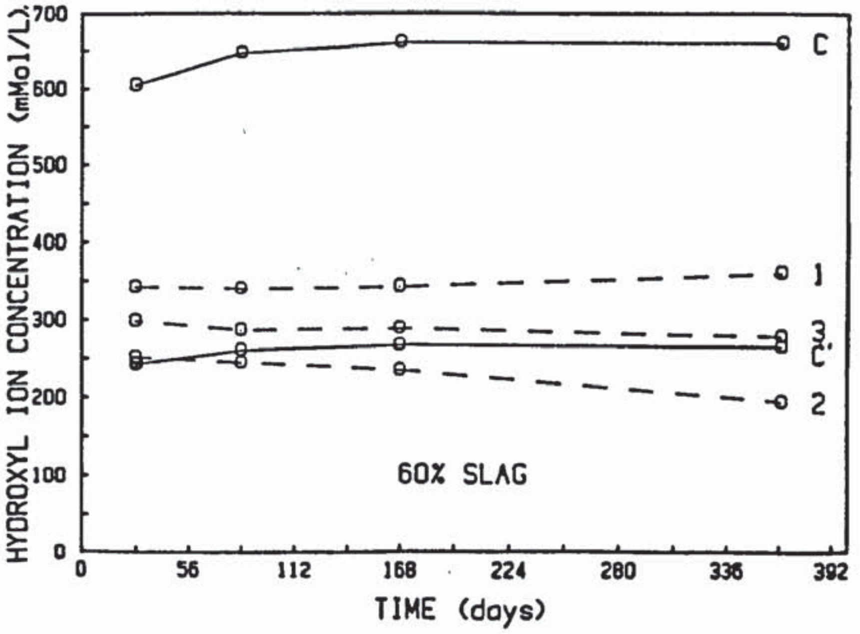

FIG. 4
Hydroxyl ion concentrations in pore solutions of Portland cement paste (C) and blended pastes containing 60% various GBFS's (1,2,3) or 60% hypothetical cement of zero alkali content (C').

Conclusions

1. PFA's, when blended with Portland cement of moderate alkali content, are generally capable of reducing the concentrations of hydroxyl ions in the pore solution phase to a greater extent than would be expected if they were assumed to behave as cement of zero alkalinity.

2. The reduction of alkalinity of the pore solution caused by PFA proceeds over a relatively long time,which suggests that it is probably associated with the incorporation of alkalis into CSH gel formed by the slow pozzolanic reaction.

3. The alkali content of PFA is an important factor governing its ability to remove hydroxyl ions from the pore solution phase of blended cement pastes but the fineness/pozzolanicity of the ash may also have a limited effect.

4. GBFS's, when blended with Portland cement of moderate alkali content, tend to reduce the hydroxyl ion concentration of the pore solution phase but generally to a lesser extent than would be expected if they were assumed to behave as cement of zero alkalinity.

5. The effectiveness of GBFS's in lowering the hydroxyl ion concentrations of cement pore liquids is not primarily controlled by the alkali content of the slag and it appears that other factors influencing the nature and composition of the CSH gel formed may be important.

6. Whilst the work described in this paper has been concerned exclusively with the role of cement replacement materials in modifying the alkalinity of the pore solution phase, it is recognised that other characteristics of the materials, such as their influence on matrix permeability, may also contribute to their effects in controlling expansion associated with ASR.

Acknowledgement

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